STAINLESS IRON AND STEEL

BY

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LONDON
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11 HENRIETTA STREET, W.C.2.
• 1931

TO MY WIFE

PREFACE

The publication of a book devoted entirely to the consideration of what is popularly supposed to be a single type of steel may at first sight need some justification. The popular notion as to the single character of stainless steel, however, is much more noteworthy for its persistence, in spite of propaganda to the contrary, than for its accuracy. One of the main points of the author's work has been to emphasise the range of diverse materials included in the term "stainless steel" which permits such widely varying properties to be obtained from different types of this material. Such a wide range of materials and available properties is of great advantage to the potential user, more particularly the engineer, but it also entails the necessity of discriminating between various types of the steel in order that the most efficient use may be made of the material for any particular purpose. It has been the author's endeavour to present data pertaining to the various grades of the steel in as clear a manner as possible, in order to aid the user in making a choice of suitable grades for varying requirements.

One of the benefits of the modern study of metallography lies in the possibility it affords of indicating which treatments, thermal or otherwise, are likely to improve the properties of a metal and why such improvements occur. In the application of stainless steel, the study of the microstructure is of especial value as the observations indicate not only the cause of varying mechanical properties but also reasons why the materials offer varying resistance to corrosion. As it is desirable that the user of stainless steel should know how he may obtain the best qualities in this respect from the material he uses, the author has dealt rather fully with microstructural characteristics, and in order that the account may be informative to those who have not

specially studied metallography, he has endeavoured to write in the simplest terms.

It has been objected on more than one occasion that " stainless steel " is not a strictly accurate description of the qualities inherent in the material. One may quite admit this and agree that " unstainable " or " corrosion-resistant," for example, would be more appropriate names. "Stainless steel," however, has become so universally adopted as a designation of the materials described in this book that the substitution of another more accurate name would be a doubtful advantage.

During the five years which have elapsed since the publication of the first edition of this book, the metallurgy of stainless steels has developed very rapidly. Much research has been carried out into the structure and properties of steels containing large amounts of chromium together or not with other metals, nickel, copper, tungsten and the like, and a considerable number of new types of " stainless steel " have been put on the market. The author, in endeavouring to deal in a systematic manner with these new developments and to present a picture of the present state of the art, found it necessary to re-draft the book, and re-write it almost entirely. The book has, unfortunately, been out of print for over three years, and the author regrets that the appearance of the second edition has been delayed for so long a time.

The author would again thank the Directors of Messrs. Brown, Bayley's Steel Works, Ltd., for permission to publish, freely, data obtained in the research laboratory and the works, and also for their encouragement during the preparation of the book. He would also thank all his colleagues who have so freely given him of their help and experience; particularly would he mention Mr. R. Waddell (Works Manager) and Mr. F. C. Bell (Engineer) for much information regarding engineering uses and Messrs. H. Bull, A. Flint, F. D. Gordon and W. Heppell for assistance in proof reading and preparation of diagrams.

J. H. G. M.

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CHAPTER I

INTRODUCTORY AND HISTORICAL

The general rusting of iron and steel which occurs whenever these metals are left for any length of time either exposed to the atmosphere or to water, or buried in the ground, has been accepted almost as a matter of course. Thus it has been stated* " The tendency to rust is a characteristic inherent in the element known as iron, and will, in all probability, never be entirely overcome." Iron rusts and there is an end of it ! If, owing to care and suitable protection, it is preserved over a long period of time, the achievement is looked upon as something out of the ordinary. It is recorded that when the first batch of stainless steel knives were being forged, the Sheffield cutler, on being told that the knives would not rust, expressed his opinion of such foolishness in strong " Sheffield," the meaning of which is quite unmistakable though the language is hardly printable.

The gradual corrosion of iron and steel entails enormous expense when considered in the aggregate. Everyone is familar with its effects on various household articles and fittings, but the expense entailed by corrosion is realised more easily when its effects on big engineering structures are considered. On the Forth Bridge, for example, painting is going on continuously from year end to year end. (Estimates have been made, at different times, of the losses caused by the rusting of iron and steel work and, if a survey of the whole world is taken, the cost reaches very large figures. Thus, Sir R. A. Hadfield† concluded that the annual cost owing to corrosion all over the world was over £700,000,000.) While such figures are possibly more in the nature of a guess, though probably guided by sound judgment, and hence only to be accepted with a considerable amount of reserve,

* " The Corrosion and Preservation of Iron and Steel," Cushman and Gardner, 1910.

† " Corrosion of Ferrous Metals." Proc. Inst., C.E., 1922

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they indicate(that the annual losses due to the gradual corrosion of iron and steel reach enormous figures.)

Apart altogether, however, from the question of expense, corrosion causes other troubles. In many engineering applications, the unsuspected corrosion·of some part of, for example, a bridge may so seriously weaken the strength, of the corroded part that it can no longer carry the load to which it is subjected and its failure, either by fracture or distortion, may have disastrous results on the whole structure. The trouble and loss of time occasioned by such breakdowns, apart from their cost, are serious items. (For household and other purposes where polished fittings or utensils made of steel are used, the necessity for frequent polishing entails a considerable amount of work, which would be avoided if the surface did not corrode.

In the chemical trade, corrosion frequently causes great trouble due not only to the gradual deterioration of the equipment but also to the contamination of the manufactured article either by the products of the corrosion of the vessels in which it is made or stored, or as a result of catalytic action by the material of which these vessels are constructed) Generally the evil of contamination is of far more moment than that of deterioration of equipment. It has been said, and truly, that the problems connected with a chemical process cannot be considered as being completely solved until a satisfactory container has been found in which the process may be carried out on the required commercial scale ; not infrequently the commercial application of some valuable process is held up for a considerable time—sometimes indefinitely—because no really satisfactory containing vessel is forthcoming. Ordinary iron and steel are in many ways particularly suitable for the manufacture of chemical plant ; they are easily worked and are obtainable in forms possessing a wide range of mechanical properties. Unfortunately, however, the ease with which they are attacked by many chemical products either limits their use or makes essential some form of inert covering, such as enamel or glass. Probably the main reason why iron and steel vessels are used to so large an extent in the chemical industry at the present time is because of their relative cheapness. It is thought to be cheaper to use them and to renew the plant frequently than to employ a more resistant but also more expensive metal.

It is obvious, however, that this is not a satisfactory con-
dition of affairs and that the advent of a metal which, though
possibly costing ten or twenty times as much as mild steel,
was immune from attack under the conditions of some
specific chemical·process would effect such economies in that
process as would make the use of this metal preferable in
spite of its greater initial cost. (Although special corrosion-
resistant steels or other alloys would seem to have been
somewhat neglected in the past by the chemical industry,
attention has recently been focussed on them, particularly
with regard to the newer synthetic processes which frequently
involve the use of high temperatures or pressures or both.
In more than one case, during the past few years, the com-
mercial success of a process has been attained only when the
equipment was constructed from some special resistant alloy.

It is not surprising, therefore, that many efforts have
been made to minimise or overcome corrosion troubles.
In some cases, for example, alloys of copper are used
instead of steel or iron, owing to their superior resistance
to general corrosion or to the attack of some particular
chemical.   There are many cases, however, where the
mechanical properties desired can be obtained only
by the use of some type of ferrous metal.   In such
cases, if a bright surface is required, either a con-
siderable amount of energy must be expended at frequent
intervals in polishing the article, with consequent wear of
the latter, or else it must be covered with some type of
transparent varnish or lacquer) Obviously the latter method
cannot be satisfactory in many cases.   (A metallic surface
more or less permanent in character may also be obtained by
tinning or galvanising or by electro-plating with some metal
which is resistant, to a greater or less extent, to corroding
agencies.) When a polished or metallic surface is not
necessary, there are other methods of protection available,
such as painting, covering with an adherent coat of magnetic
oxide of iron (e.g., by the Bower Barff process or its modifica-
tions or by the Ruffington process) or the production of a
phosphatic coating such as that obtained by the Coslett
process.   Coatings of enamels of various types or linings
of glass may be used, as for example, in chemical equip-
ment or domestic utensils.

(All such methods, while of great value for many

purposes, have obvious disadvantages in certain important respects. Some of the coatings are brittle and, therefore, liable to chip off, while in all cases the application of the protective coating must be the last stage in the manu- facturing process ; no further drilling, sawing or any other type of machining should be done after the coating is applied, or the continuity of the latter will be broken and an un-protected surface of the iron or steel exposed.) From an. engineering point of view, a coating of any description has an even more serious drawback in that the protection it gives is entirely superficial in character and is, therefore, of little lasting value if the article to which it is applied is subjected during use to any type of rubbing or wearing action or if a cutting edge is required.   In such cases the method employed to render the iron and steel satisfactorily resistant to corrosion must not be confined to the surface only, but must be incorpor-ated in the body of the material so that, as the outer surfaces are worn away, the new material exposed shall be equally resistant.   Such a quality of resistance can only be effected by altering the properties of the whole mass of the steel and the only possible way of doing this is by alloying the steel with some other metal which shall have the power of preventing the alloy produced from being attacked · by corrosive agencies.

The possibility of retarding the corrosion of iron and steel by the addition of other metals has been recognised for many years and some alloys having marked resistance to corrosion were discovered a number of years ago.   Probably the best known examples are the high nickel steels, containing 25 to 35 per cent. nickel.   These steels, though by no means incorrodible, resist corrosion to a very much greater degree than ordinary steel and have been used to some considerable extent.   They are rather expensive, however, and their mechanical and physical properties are not suitable for all purposes ; for example, they cannot be hardened by quenching or by any other form of treatment which can be applied to an article possessing approximately its final shape and dimensions, while in no case can they be given a hardness value anything approaching that required for a cutting tool.

At the time when these high nickel steels were put forward as corrosion-resisting metals, it was customary to employ solutions of sulphuric acid as test reagents and to

regard the rate of attack of these solutions on the various steels as a measure of the rates of corrosion of the latter. It was considered that tests carried out with this acid, owing to its much greater corrosive action as compared with water, would enable results to be obtained in a short time but would nevertheless place the metals tested in the same order of merit which they would occupy if subjected to a much more prolonged action of water or of the atmosphere. It has since been abundantly proved that the attack of sulphuric acid, or of other acids, on a series of different metals or alloys, is not always comparable with that of water or of the atmosphere and that the use of such accelerated tests is very likely to lead to erroneous conclusions. The high nickel steels mentioned above, as it happens, are very resistant to the attack of sulphuric acid and it is very likely that their vogue as non-corrosive steels arose largely because the measure of corrosion adopted at the time was the response of metals to the attack of this acid.

Another iron alloy having resistance to special forms of corrosion contains about 12 or 14 per cent. of silicon and is sold under various trade names. This material is attacked extremely slowly by mineral acids. Owing to its nature, however, it is more or less allied to cast-iron, hence its use is restricted to purposes for which its mechanical and physical properties are suitable; thus it is comparatively brittle, it is so hard as to be machinable with difficulty, if at all, and it cannot be forged or rolled.

It will be seen, therefore, that there is an immense field for a steel product which possesses the property of great resistance to corrosion in each and every part of the articles which may be manufactured from it, and which also has a wide range of physical and mechanical properties comparable in extent with those found in the material known to-day as " steel." Such a non-corrosive material is now available in the range of alloys known collectively as " Stainless Steel."

Stainless steel was first introduced to the public in 1914 in the form of table cutlery and its almost exclusive use for cutlery purposes for a considerable period of time after that date led to the belief, probably widely held, that it was simply a special type of cutlery steel with a very limited range of mechanical properties. It was even

considered to be a special form of plating. Had this been so, stainless material would have had a very limited application and it would not be of great interest to engineers. Fortunately, however, this is not the case. Stainless steel is really a whole series of steels, whose mechanical and physical properties vary widely in a similar manner to the variations met with in the different varieties or " tempers " of ordinary carbon steels, but which all have the distinguishing property of great resistance to corrosion conferred on them primarily by the presence of a considerable percentage of chromium. As a general rule, the amount of this element present in stainless material is in the range 12 to 20 per cent., but less or more may be added for special purposes.)

In ordinary steels, variations in the mechanical properties of the material are controlled largely by the presence of varying amounts of carbon ; thus very mild or soft steel may contain 0·10 per cent. carbon or less, while for certain types of tool steel 1·6 to 1·8 per cent. is occasionally added. These values represent extremes and intermediate amounts are chosen to give properties suited for definite purposes. So in certain types of stainless steel, variation in mechanical properties is brought about largely by the presence of varying amounts of carbon ; in this case, however, the range of carbon content, for reasons which will be seen later, is much more restricted so that, as a general rule, the carbon content of stainless material is not more than about 0·4 per cent. Still further variations in the properties of the steel may be obtained by the addition of other alloying metals. Generally speaking, this is done for the purpose of increasing the resistance of the steel to the attack of some particularly corrosive reagent or group of reagents ; frequently the added metal also modifies the mechanical and physical properties of the steel. For example, additions of such metals as copper, nickel, silicon, molybdenum, tungsten and cobalt, either singly or in combination, have been recommended for one or other of these purposes and in some cases at least have given remarkable results. The development of such " alloyed " stainless steels is probably as yet only in its infancy.

The resistance to corrosion of such high chromium steel was discovered by Mr. Harry Brearley in 1918. Mr. Brearley was then chief of the Research Laboratory run jointly by Messrs. John Brown & Co., Ltd., and

Messrs. Thomas Firth & Sons, Ltd., Sheffield. He was at the time engaged on an extensive research on the resistance to erosion of various steels in reference to their use for rifles and naval guns. Among the steels examined for this purpose, were some containing large amounts of chromium. In the course of these investigations, numbers of samples, in different conditions of heat-treatment, were examined microscopically as is, of course, usual in such investigations. In carrying out this examination, Mr. Brearley noticed that these high chromium steels were either not etched at all or only attacked very slowly by the reagents generally used for etching the polished surfaces of sections of steel prepared for microscopic examination and that, moreover, they did not rust when exposed for considerable periods to the atmosphere of a physical laboratory. He also found that, both with the usual microscopical reagents and also with new types developed for the purpose, the same steel under different conditions of heat treatment would sometimes etch and sometimes not etch, thus indicating that the resistance of the steel to various forms of chemical attack was affected by heat treatment. He was struck with these marked characteristics and proceeded to investigate, on the one hand, the limiting ranges of composition for producing a steel practically resistant to ordinary corrosion and also the conditions of heat treatment necessary with any particular steel for developing to the greatest extent this resistance to corrosion.

The many possible uses of such a material having very great resistance to corrosion were evident to Mr. Brearley, and one of the most obvious purposes where it was likely to be very useful was that of cutlery. At first there was some difficulty in getting the material tried but eventually, about the middle of 1914, Mr. Brearley was able to persuade Mr. E. Stuart, cutlery manager for Messrs. R. F. Mosley, of Sheffield, to work up some of the steel into knives. The results were strikingly successful in spite of initial difficulties, due largely to the best conditions of forging and working the steel being different from those of ordinary cutlery steel. In this respect very great credit is due to Mr. Ernest Stuart for the unremitting efforts he made to adapt the processes of knife making to the unusual qualities of the steel and to Messrs. R. F. Mosley for realising the possibilities of the material and possessing such confidence in it as to

allow their works to be used for this pioneer experimental work.

Early in 1915, Mr. Brearley severed his connection with Messrs. Brown's and Firth's and became Works Manager at Messrs. Brown, Bayley's Steel Works, Ltd. Owing partly to lack of time, due to pressure of work in his new position, and for other reasons, no application was made for a British patent, but in August, 1915, a patent was granted in Canada, followed in September, 1916, by a further patent in the United States of America (and also by patents in other countries), for a stainless article which owed its special stainless properties to three novel features :

(a) That its chemical composition was within certain well-defined limits ;
(b) That it had been heat-treated to produce certain microstructural characteristics ;
(c) That it was metallically clean and in an undistorted condition.

The range of composition specified was 9 to 16 per cent. chromium with carbon below 0·7 per cent. and preferably below 0·4 per cent. Certain other elements in limited amounts, up to 1 or 2 per cent., were also allowed as not affecting the result, the elements actually specified in the patents being nickel, cobalt, copper, tungsten, molybdenum and vanadium. The U.S.A. patent applied more particularly to cutlery and other hardened and polished articles, while the Canadian patent especially embraced material which had been hardened and then tempered to a sufficient extent to be tough and ductile.

The claim with regard to structural characteristics referred to the absence or presence of " microscopically distinguishable free carbides " ; the patentee stated that these became present when the carbon content exceeded 0·7 per cent. He does not state how he arrived at this demarcation in the carbon content, but it seems possible that the value of 0·7 per cent. carbon was estimated from the appearance of small samples cooled from a molten condition. It does not apply when the steels are heat treated in the correct manner, e.g., to produce a table knife. At that time, however, the microstructure of high chromium steel and the

complexities of its heat treatment were not fully understood. The range of composition specified, however, does mark out wonderfully well the material useful for those technical purposes for which a steel capable of being hardened and tempered is desirable, and it is highly probable that, had the composition of stainless material for such purposes to be fixed at the present time with the accumulated knowledge of the past few years at the disposal of the discoverer, the range chosen would not differ materially, if at all, from that laid down in 1915.

The production of a chromium steel was not by any means new, in fact the literature of iron and steel metallurgy during the nineteenth century and the first ten years of the present century contains many references to the preparation of chromium steels and to some of their physical properties. Several comparatively extensive investigations into the properties of chromium steels had been carried out, notably those of Hadfield, Guillet and Portevin, but the remarkable point is that neither these investigators or any others prior to 1910 appear to have had any idea that high chromium steels with a composition approaching that of stainless steel, were so remarkably resistant to corrosion. In most cases, no study of the effect of chromium on the rate of corrosion had been made, while in one notable case, that of Hadfield,* in which such experiments were carried out, though to a very limited extent, the results indicated, as will be seen later, that the rate of corrosion actually increased with increasing content of chromium. Guillet who carried out an extensive investigation on the effect of chromium contents up to about 30% on the properties of steel, was apparently quite unaware of their almost unique characteristic. Thus, in summarising the results of his work on these steels he says† : " Chromium steels are little used in construction work (we only speak here of the ternary alloys, Fe-C-Cr.) ; they are used in the manufacture of armour-piercing shell, which contains 0.80 per cent. carbon and 2 per cent. chromium. Further, in view of the great hardness of the martensite, chromium steels with low chromium content and a high percentage of carbon are used as tool steels. Will this study provide new outlets for chromium steels ? We do not think so. Only the pearlitic

*J.I.S.I., 1892, II, 48.
†Genie Civil, March, 1904.

steels are of some interest, but all other things being equal, their resistance to impact is inferior to that of nickel steels and they are more difficult t） work.

" Martensitic steels have an extreme hardness ; they could only be used as tool steels, as such they could be used simply as forged but they are difficult to work.

" As to double carbide steels, their brittleness and their extremely high price make all application impossible.

❨ We do not see any important outlets for chromium steels. But it must be admitted that this metal (chromium) gives steel a special characteristic and plays a part which could not be taken by another substance ; it causes an important mineralogical hardness if the percentage is not too high.❩

It is not necessary to give a detailed account of the many investigations on chromium steels which do not deal in the slightest degree with the effect of this metal on the corrodibility of the steel. For those interested in the early history of chromium steel, a good summary of such investigations will be found in Hadfield's paper mentioned earlier. It is of interest, however, to review briefly the few papers or articles in which some reference is made to corrosion or to the resistance of the metal to attack by acids.

The earliest reference, with which the author is acquainted, to the influence of chromium on the corrodibility of iron or to the rate of its solution in acids is in an article by Berthier,[*] dealing with alloys of chromium with iron and with steel. Berthier stated that ferrochromium is much less readily attacked by acids than iron, the more so the more chromium it contains.

At about the same time, Faraday and Stodart carried out an extensive series of experiments on the effects of adding various metals to iron and steel. They had definitely in mind the subject of the corrosion of steel and the possibility of retarding it. Thus in the accounts[†] given of their work, they state : "The object in view was two-fold : first, to ascertain whether any alloy could be artificially formed, better, for the purpose of making cutting instruments, than steel in its purest state ; and secondly, whether any such

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[*] *Annales de Chimie et de Physique*, 1821, Vol. 17, p. 55.

[†] " On the Alloys of Steel." Stodart and Faraday. Quart. *Journal of Science*, Vol. IX, p. 319. *Phil. Trans.*, 1822, p. 253.

alloys would, under similar circumstances, prove less susceptible of oxidation; new metallic combinations for reflecting mirrors were also a collateral object of research."

Their preliminary work was done on small samples melted in crucibles at the laboratory of the Royal Institution, but later, they had larger amounts of some of the alloy steels melted at one of the crucible steel works in Sheffield. Faraday and Stodart experimented with silver, platinum, rhodium, palladium, iridium, osmium, gold, tin, copper and chromium, and all except the last four metals were used in the larger scale experiments at Sheffield. Apparently Faraday and Stodart only made two small experimental melts of chromium steel, which probably contained rather less than one per cent. and three per cent. respectively, and their observations on the resulting steels were concerned chiefly with a beautiful damasked surface which they obtained by etching with dilute acid or by a form of heat tinting. They do not comment on the resistance of chromium steels to corrosion except to remark that, in common with a number of other metals, chromium increased the rate of attack of dilute sulphuric acid on the steel.

The experiments of Faraday and Stodart are noteworthy in that they appear to be the first systematic attempt to make alloy steels and to study their properties. They did not discover the corrosion resisting properties of high chromium steels though they found that some of the alloys of platinum and iron were noteworthy in this respect. Unfortunately this discovery has not much commercial value, especially at the present time.

The next one in order of date appears to be a paper by Robert Mallet,* on " The Action of Water on Iron," in which he states that alloys of iron with any of the following elements, nickel, cobalt, tin, copper, copper and zinc, mercury, iridium, osmium, columbium, and chromium are less corrodible than iron, and of these alloys that of chromium is least corrodible. He states, however, " with a metal positive to it (like chromium), though it may possibly protect the iron from action, will, by its own removal, be likely to render its texture open and course and, hence, more fitted for its subsequent solution and removal." It appears as if Mallet's idea was that the resistance to corrosion

* B.A. Report, 1838, Vol. VII, p. 265.

of iron containing chromium was, at the commencement
of exposure, increased by the presence of the chromium, but
that the chromium was first removed by the corroding
agency and that after this had occurred the remaining iron
would be more quickly corroded than if the chromium had
not been·present.

In an article by Fremy* on crystallised·chromium and·
its alloys, it is stated that " Chromium crystals resist the
action of the strongest acids and even of aqua regia.". It
should be noted that these crystals could not possibly have
been pure chromium or even carbon-free iron-chromium
alloys. They were almost certainly highly carburised.
Fremy also remarks that he has noticed alloys of chromium
frequently resist the action of concentrated acids. The
greater resistance of iron-chromium alloys to attack of acids
as compared with that of iron was also noted by Boussingault.†
By·this time analysts, who handled such alloys, knew that the
ferrochrome which they analysed and which contained large
amounts of carbon, could not be dissolved by the usual acids.·

In 1872, Woods and Clark applied for a British patent‡
for a metal to resist acids and which would also retain its
polish in a damp or oxidising atmosphere. The metal
contained about 30 or 35 per cent. chromium together with 1·5
to 2·0 per cent. tungsten. The carbon content was not specified
but as the alloy was to be made by fusing the constituent metals
in the presence of carbonaceous matter and either a crucible
or a blast furnace could be used for preparing it, there is
little doubt that the product would be highly carburised and
more in the nature of a cast iron than a steel.

Gruner§ studied the capacity of resistance of various
steels to the influence of air, sea-water and acids. His
opinion on a chromium steel is summarised at the end of
the report in the following words : " The presence of
chromium favours corrosion by acidulated water as well as
by humid air and sea-water."

In 1892, R. A. Hadfield published the results of an
extensive investigation on chromium steels‖ which also

* *Comptes Rendus*, 1857, Vol. 44, p. 632.

† *J.I.S.I.*, 1886, II, 807.

‡ No. 1,923, June 25th, 1872.   Provisional protection only was obtained.·

§ *Annales des Mines*, 1883, I.

‖ *J.I.S.I.*, 1892, II, 48.

included a few corrosion tests. These latter, however, were carried out by exposing the samples to the attack of fifty per cent. sulphuric acid, the assumption being made apparently, as was usual at the time, that such an acid test would give results in the same order as those given by ordinary corrosion tests but at a greatly accelerated rate: Hadfield's results showed that as the chromium rose from 1·18 per cent. to 9·18 per cent., the rate of attack increased very decidedly. It is noteworthy that Hadfield does not comment in his paper on these results nor does he refer to any other corrosion tests. In an Appendix to Hadfield's paper, Osmond contributed a description of the microstructures of some of Hadfield's steels. He noticed that in those containing 5·19 and 9·18 per cent. chromium, the microstructure, in some cases, showed the presence of minute particles, presumably carbide, which were not attacked in the least by the etching reagent used, 20 per cent. nitric acid.

 . What appears to be the only reference to the relative effect of carbon and chromium on the resistance to acid attack of iron alloys is contained in an article by Carnot and Goutal, " On the Condition of Silicon and Chromium in Metallurgical Products."* These investigators found that chromium steels containing a small amount of chromium are • readily attacked by acids (even when cold and diluted) if they are highly carburised, but much more slowly and with greater difficulty when they contain a small amount of carbon.

Hadfield's results as to the increased corrodibility of chromium steels in sulphuric acid were confirmed by Monnartz†, who also found similar results with hydrochloric acid. Monnartz also found that the behaviour of chromium steels with respect to nitric acid was more complex. Up to 4 per cent. chromium, the resistance to dilute nitric acid decreased as the chromium increased, while, on the other hand, the resistance to concentrated nitric acid increased. Above 4 per cent. chromium, the resistance to dilute nitric acid rapidly increased as the chromium rose to 14 per cent. and more slowly afterwards, until at 20 per cent. chromium the alloys were as stable as pure chromium. Monnartz's work was concerned mainly with the resistance of the alloys to acids.

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* *Comptes Rendus*; 1898, Vol. 126, 1243.

† *Métallurgie*, Vol. VIII, 1911, p. 161.

He mentions, however, that the higher chromium alloys, especially those containing over 40 per cent. chromium, showed excellent stability towards atmospheric conditions. Thus he states that such alloys, which were exposed for two years to the influence of the laboratory atmosphere, showed no trace of change, retaining their original bright lustre. They were also stable in a remarkable manner to river-water; in addition, the high percentage alloys resisted cold sea-water well, while those containing less chromium were attacked. Monnartz, however, does not give any details as to which alloys (his series included alloys up to 98 per cent. chromium) were or were not successful; in fact the remarks as to atmospheric and water attack are introduced almost casually at the end of the section of the article dealing with the resistance of the alloys to nitric acid.

Monnartz also experimented with iron-chromium-molybdenum alloys and the results of his investigations led to the German patent 246,035 (Jany. 22, 1910), in which his name is coupled with Borchers', for an iron alloy which combined high resistance to chemical action with mechanical workability and which consisted of an iron-chromium alloy to which was added 2 to 5 per cent. of molybdenum, vanadium or titanium. The minimum chromium content of the alloy is given in the patent as 10 per cent., but it would appear that the inventors had in mind the use of much higher amounts than this, as the only composition specifically referred to was one consisting of about 60 per cent. chromium, 85 per cent. iron and 2 or 8 per cent. molybdenum.

Finally the corrodibility of a series of steels containing up to 5·3 per cent. of chromium (along with other alloy steels) was examined by Dr. Newton Friend,* who found that his results confirmed those of Hadfield as to the resistance of such steels to the attack of sulphuric acid. As regards the resistance to neutral corroding media, he states that in such media "the resistance offered to corrosion apparently rises with the percentage of chromium. This is particularly the case for salt water, and the employment of chromium steels in the construction of ships would appear to be fully justified on this ground alone." In connection with this, it should be noted that Friend did not experiment with any steel

* *J.I.S.I.*, 1912, I, 249; 1913, I. 388.

containing more than 5·3 per cent. chromium, an amount quite insufficient to reduce the corrosion of the steel in neutral media to negligible amounts and that, although he found the amount of corrosion to be considerably reduced by the presence of this content of chromium, such steels still corroded to a quite considerable extent.

It will thus be seen that at the time of the discovery of the remarkable non-corrosive properties of the material subsequently known as "stainless steel," the published information on chromium steels would not have led anyone to suspect that such remarkable properties were likely to be present. Broadly speaking such knowledge as there was indicated that : —

(a) Iron-chromium alloys containing large amounts of chromium resisted the attack of certain strong acids. These alloys were almost certainly very highly carburised and hence had mechanical properties akin to cast iron rather than to steel.

(b) The addition of chromium decreased the resistance of steel to the attack of sulphuric acid. It should be remembered that such tests were believed to indicate the general corrodibility of the several steels in other media, and hence gave the impression that chromium steels were not likely to be of much value as non-corrosive materials.

(c) It had been shown that the presence of chromium up to about 5 per cent. retarded the corrodibility in neutral media. The investigations, however, did not indicate the influence of the carbon content, nor of the heat-treatment of the steel (or of other points which, as will be shown later, have a decided influence on the non-corrosive properties), nor did they suggest that it was likely that a steel practically immune from corrosion could be developed.

(d) Monnartz' work showed that "high chromium alloys" (especially those with 40 per cent. chromium and upwards) resisted atmospheric attack and river and sea water.

It is therefore clear that the discovery of the non-corrosive properties of chromium steel by Brearley, in 1913, was something entirely new in the history of these steels.

As frequently happens however, in scientific discovery, other investigators had been working quite independently, and at about the same time, along somewhat similar lines. In the United States of America, Elwood Haynes, several years prior to 1912, had experimented with cobalt-chromium and cobalt-chromium-tungsten alloys and as a result had patented and put on the market a series of alloys, known collectively as " Stellite," from which tools were made considerably superior to those of the best high speed steel, as regards their ability to cut when hot.   In addition, these alloys were remarkably resistant to corrosion.   Further experiments involved, among other things, the addition of iron to the alloys and led to the discovery that the ternary cobalt-chromium-iron alloys were more malleable than those free from iron and to a degree increasing with the iron content. At the same time, the corrosion-resisting properties were good, providing the alloy contained not less than 10 per cent. chromium and 5 per cent. cobalt. Haynes named the ternary alloy " Festel " metal and its properties led him to investigate iron-chromium alloys free from cobalt.   He published an account of his experiments in 1919* and from this, it would seem that during 1911 and 1912, he made some small ingots, weighing probably about four ounces each which, from the constituents of the mixtures melted, probably contained from 5 to 20 per cent. chromium.   From these ingots were hammered small tools which were found to function well in this capacity ; they also resisted atmospheric corrosion extremely well.   It is difficult to judge to what extent Haynes followed up his discovery but, from what he states in the paper mentioned above and also in a later one published in 1921,† it would appear that he was concerned mainly in the properties of the alloys from the point of view of cutting tools, that he was not particularly interested in the effects of heat treatment on the alloys and that he knew little about either the range of physical properties obtainable from high chromium steels by means of suitable heat treatment or the relative effects of carbon and chromium both

* *Proc. Eng. Soc. Western Penn.*, Vol. XXXV; p. 467.

† *Yearbook, Amer. Iron & Steel Inst.*, 1921, p. 21.

as regards response to heat treatment and resistance to corrosion. · It is at least certain that the commercial development of the high chromium steels took place some considerable time later in the United States than in Britain.* Haynes tells us that his first application for a patent was rejected on the ground that chromium steels were not new. In this connection it is interesting to note that he remarks, in the earlier paper referred to above, that after making his initial experiments, " In order to make sure that such alloys were unknown at this time, letters were written to practically all the large steel producers of the United States, asking for a non-rusting or non-tarnishing iron or steel alloy, but the replies received were all of a negative character, and showed that no such alloy existed, but suggested the possible use of alloys of nickel and iron, but in no case was chrome-iron or chrome-steel even mentioned." It is perfectly clear therefore that the steelmakers of the United States of America, as a whole, and probably those of other countries in general as well, were then ignorant of the special non-rusting ·characteristics of high chromium steels. This is important, as attempts,† not very satisfying it must be confessed, have been made to suggest that such a characteristic of high chromium steels was well known.

Haynes filed a second application for a patent in 1915, actually fifteen days before Brearley filed his. Haynes' patent was not granted, however, until 1919; it claims alloys of iron and chromium containing not less than 8 per cent. (and preferably 10 per cent.) and not more than 60 per cent. of chromium as being specially resistant to corrosion. The carbon content was to be not more than 1 per cent. and preferably in the range of 0·1 to 0·5 per cent. He particularly mentions alloys containing 80/75 per cent. iron, 20/25 per cent. chromium and 0·1/0·5 per cent. carbon as being well adapted for the purposes of his invention. He says " such an alloy is hard, stiff and strong, has good ductility, works well under the hammer and swages readily, has a high

* Dr. J. A. Mathews (of the Crucible Steel Co. of America), stated in the discussion of Haynes' paper, in 1921 : " We pride ourselves on being a progressive people, yet in the matter of adopting stainless steel for general use we are far behind our conservative British cousins. The use of stainless steel in Great Britain in its various applications has gone ahead very much more rapidly than it has in America."

† See, for example, " Corrosion-Resistant Alloys—Past, Present and Future." P. A. E. Armstrong. *Proc. Amer. Soc. Test. Mat.*, Vol. XXIV, Pt. 2, 1924.

lustre, taking an excellent polish and will take and retain a good smooth permanent cutting edge, readily renewable by honing and grinding." In view of these remarks and of the fact that he specifically states that his alloys are particularly suitable for cutlery, it is interesting to note that the greater part of the material included in this particular range of composition (80/75 per cent. iron, 20/25 per cent. chromium, 0·1/0·5 per cent. carbon) cannot be appreciably hardened by quenching from any available temperature ; see pp. 59, et seq.

In Germany, Drs. Strauss and Maurer, of the research department of Messrs. F. Krupp, A.G., had turned their attention to the joint effects of chromium and nickel on steel. A preliminary note on their investigations was published in June, 1914, in a paper* read by Dr. Strauss before a meeting of chemists at Bonn. The paper dealt with the microscopic examination of steel but in it reference was made to the marked rustlessness and acid resisting properties of steel containing large amounts of chromium and nickel. A detailed account of their work does not appear to have been published until August, 1920† ; here the authors state that their studies of these high chromium-nickel steels were conducted between 1909 and 1912. In October, 1912, patents were obtained in Germany, and later in other countries for two series of chrome-nickel alloys for which corrosion resistant properties were claimed. In the first series,‡ for resistance to general corrosion (not acids), the limits of analysis were 0·5 to 20 per cent. nickel, together with 7 to 25 per cent. chromium. The second series,§ comprised alloys containing 4 to 20 per cent. nickel with 15 to 40 per cent. chromium and, for these, resistance to attack by acids, particularly nitric acid, was claimed. In both series of steels the carbon content was limited to 1 per cent. or less. It will be noticed that in both patents, nickel is included as an essential constituent of the steels ; it would appear in fact, from the published accounts, that Drs. Strauss and Maurer were not aware of the excellent properties

· * Z. Angew. Chem., Vol. XXVII, pp. 633-645. Stahl u. Eisen, 1914, p. 1814.

† " Die Hochlegierten Chromnickelstahle als Nichtrostende Stahle." Kruppsche Monatshefte, August, 1920.

‡ German patent 304,126. Oct., 1912. British patent 13,414. June, 1913.

§ German patent 304,159. Dec., 1912. British patent 13,415. June, 1913.

possessed by the pure chromium steels.   In this connection
one may note that a third English patent (No. 13,413) was
obtained at the same time as the two mentioned above, for
steels containing 15/25 per cent. chromium (which could be
partly replaced by nickel if desired) ; in this patent, resistance
to oxidising conditions at high temperatures, e.g., 700°/1000C.°
was claimed, but no mention was made of resistance
to general corrosion.   As a result of these patents,
Messrs. F. Krupp, A.G., placed on the market two types of
steel, one, termed " V.1.M.," containing 12/14 per cent.
chromium and 1·5/2·0 per cent. nickel and the other, "V.2.A."
containing about 20 per cent. chromium and 7 per cent.
nickel.   In the latter case, the nickel content is undoubtedly
a determining factor in the mechanical and corrosion-resisting
properties of the steel ; as will be seen later, this material
differs markedly in many respects from the Brearley type
of stainless steel.   The " V.1.M." steel, however, corresponds
closely to Brearley's steel, but it is very doubtful if the
1·5/2·0 per cent. nickel, which it contains as an essential
constituent, has any appreciable influence on the resistance
of the steel to corrosion ; and such effects as it has on the
mechanical properties are in many cases disadvantageous
rather than otherwise.

Modern rust-resisting steels thus owe their conception
to at least three sources, and it seems quite evident that all
the discoveries were made independently of each other.
Often however the value of a discovery lies in its adaptation
to human use—it is largely considerations of this nature
which distinguish " discovery " from " invention "—and in
this case one can narrow the issue somewhat.   As regards
steels containing only chromium, although their property of
resistance to corrosion was discovered almost simultaneously
by Brearley and Haynes, it is to the former almost entirely
that their adaptation to engineering and technical purposes
is due.   It may be said quite definitely that the type of
stainless steel which depends for its properties on the presence
of chromium alone, had its commercial birth in Sheffield
and was largely reared there.

On the other hand, the credit for the chromium-nickel
type of stainless steel, and particularly where the nickel
content is sufficiently high to produce what is known as an
austenitic alloy (the type named by Messrs. F. Krupp

" V.2.A."), undoubtedly goes to Drs. Strauss and Maurer. Goods made from this alloy (and also " V.1.M.") were exhibited by Messrs. F. Krupp at the Malmo Exhibition in April, 1914, and were probably among the earliest rust-resisting steel articles made.   Their development outside Germany, and probably also in that country, was undoubtedly very largely hindered owing to the outbreak of the World War in July, 1914, so that even by 1923 or 1924 they were comparatively unknown in most countries.   Since that time, however, the " V.2.A." type of alloy has found many applications.   The usefulness of the " V.1.M." type of steel has not been so apparent however, and more recently the German firm have put on the market other brands (e.g., " V.3.M." and " V.5.M.") in which the nickel content is lowered to about 0·5 per cent., i.e., to an amount such as is often present accidentally in the Brearley steel, and thus brought them into like with the latter type of alloy.

When tracing the commercial development of stainless steel since its discovery and also its evolution from two simple types—a hardenable steel and an austenitic steel—into the numerous forms which are manufactured to-day, it should be remembered that during the first eight or ten years of this period, only the plain chromium steels of the Brearley type were made in this country ; the austenitic chromium-nickel form was not introduced until the end of 1923.   In Germany, of course, the latter steel had been employed earlier than this—though it is doubtful whether it was used to any great extent in that country prior to 1919 or 1920, owing to wartime conditions—but in the United States of America, and probably most other countries, its development was even later than in England.

At the time of Brearley's discovery, there were several varieties of ferrochromium on the market, the variable being the carbon percentage.   Chromium has a very great affinity for carbon so that it is a matter of some considerable difficulty to produce alloys rich in chromium and, at the same time, comparatively free from carbon. In the grades of ferrochromium generally available at that time the carbon ranged from about 8 per cent. to about 0·6 or 0·8 per cent.   As such alloys contained about 60 per cent. chromium it is obvious that only the lowest carbon material was of any value for producing a low carbon steel containing

about 12 per cent. chromium and also that, with this lowest carbon ferrochromium, the commercial production of a stainless steel with less than about 0·25 per cent. carbon was impossible; indeed it was quite easy for the carbon to rise to 0·3 or 0·4 per cent. during melting, owing to the avidity with which the molten material absorbed carbon.

There were certainly carbonless chromium alloys and even metallic chromium on the market; these alloys, which were produced by the Thermit process, were, however, much more expensive than the other chromium alloys and they were not being produced in any quantity. As it happened, however, the carbon content of the stainless steel produced by the low carbon alloys mentioned in the previous paragraph, i.e., in the neighbourhood of 0·3 per cent., was probably the most suitable for the production of stainless cutlery for which the material was first used commercially, so that the need for lower carbon steel was not at the time urgent. Any further development in that direction which might have taken place was held up during the period of the Great War, because the value of stainless steel for war purposes, particularly for the manufacture of valves for the engines of aeroplanes, was soon realised, with the result that the whole of the output of stainless steel in this country was taken for war purposes. Here, again, there was no particular incentive to produce a lower carbon material because, for the manufacture of aero valves, a somewhat higher carbon steel than that used for cutlery was an advantage, for reasons which will be seen later. After the conclusion of hostilities, however, opportunities occurred for developing the production of stainless steel with carbon content considerably below 0·3 per cent., and with the advent, on a reasonable commercial scale and at an economic price, of carbonless ferrochromium, the production of stainless material with 0·1 per cent. carbon or less became possible. As far as the author is aware, such low carbon stainless steel, or stainless iron as it is quite generally called, was first produced on a commercial scale in June, 1920, when the firm with which he is associated made a five or six ton cast of material containing 0·07 per cent. carbon and 11·7 per cent. chromium and cast it into twelve-inch square ingots. Similar low carbon material had certainly been produced prior to this, but only in small quantities and generally for experimental purposes only.

The physical and mechanical properties of the low carbon material thus produced were found to be ideal for a number of purposes. Thus it could be hot worked with considerably greater ease than the higher carbon stainless steel and, after suitable heat treatment, it had a range of tensile strength of the order of 30/70 tons per square inch. It was, therefore, suitable for many purposes for which the higher tensile strength of stainless steel had been rather a disadvantage.

The necessity for using a totally different raw material, carbonless ferrochromium instead of the ordinary low carbon variety (0·6 to 1 per cent. carbon), led to the idea that stainless iron was a distinct product and quite different from the pre-existing stainless steel. While this was, perhaps, true in some respects, it was quite wrong metallurgically. The name stainless iron may be commercially justifiable, but the material is more correctly described as a very mild stainless steel and forms the lowest carbon member of a series of steels of continuously varying carbon content which are, in many respects, analogous to the series of ordinary carbon steels ranging from "dead soft" to tool steels, except that in the case of the stainless material the range, as mentioned earlier, is not so extensive. Thus it is not possible to prepare stainless material commercially with a tensile strength of the same order as that of the softest carbon steels, i.e., about 25 tons per square inch or less, while at the other end of the scale it is only possible to produce the same degree of hardness in stainless steel as is associated with a fully hardened carbon tool steel by increasing the carbon content to a value which entails a considerable loss in resistance to corrosion. ' However, within the limits of tensile strength most satisfactorily available, which extend from about 30 tons per square inch up to about 110 tons per square inch, these stainless steels of the " Brearley " type may be produced in forms possessing any desired strength by suitably varying the composition and treatment of the steel.

The idea that there are different " tempers " of this type of stainless material, similar to those of ordinary carbon steel, is not yet by any means fully realised, especially in the engineering industries. This is unfortunate as, generally, the use of the proper type of stainless material for a particular purpose is as important with this material as it is with ordinary carbon steel.

The series of steels thus produced—containing 12/14 per cent. chromium and an appropriate amount of carbon for each particular purpose—were amazingly successful in many directions.   In addition to satisfying the demands of the cutlery trade, their use solved many difficult problems in connection with steam and hydraulic service.   They have been extremely valuable for turbine blading, particularly the irons and lower carbon steels whose mechanical properties are well suited to the fabrication methods employed by turbine makers.   But in certain cases, they fell short of the early optimistic anticipations of their value.   For example, the range of chemicals to which they offered a reasonable resistance proved to be less extensive than was hoped.   On the general engineering side, it was, found that, when in contact with copper alloys while immersed in water, and particularly saline water, they were liable to be selectively attacked, due to electrochemical effects between the two metals.   Corrosion proceeding from electrochemical effects is not unknown to engineers in connection with other metals ; the example of a bronze propeller inducing rapid corrosion of a ship's plates may be instanced.   Trouble of a similar nature was also experienced with the stainless material owing to contact with certain types of packings, particularly those containing graphite.

In an endeavour to improve the resistance of the steel to such forms of corrosive attack, an increase in chromium content immediately suggested itself, and actually material containing 17/20 per cent. chromium instead of the 12/14 per cent. previously used was found to possess very desirable properties from a corrosion-resistance point of view.   Thus its stability against sea water, especially in the form of spray was very much greater than that of the lower chromium steel ; also in situations where the latter showed, in the course of a few days, selective attack due to contact with copper alloys in sea water, the higher chromium alloy remained unaffected after twelve months.   Unfortunately, however, these desirable chemical attributes had been purchased at the cost of mechanical properties ; the higher chromium alloy would not harden to any useful extent when quenched unless its carbon content was raised considerably, a procedure which nullifies the beneficial effect of the extra chromium, and in addition it did not possess adequate

toughness. Experiments indicated, however, that if a small amount of nickel, about two per cent., were added to the high chromium steel, the latter regained the power of hardening and also the capacity for giving, after suitable heat treatment, mechanical properties similar to those possessed by the lower chromium steels of equal carbon content. A series of steels of this type was put on the market, under the name " Twoscore," by Messrs. Brown, Bayley's Steel Works, Ltd., during 1925 ; they are useful to the engineer in providing him with hardenable steels possessing considerably greater resistance to severely corrosive agencies than those of lower chromium content.

As has been mentioned earlier, the development of the Krupp austenitic alloys was undoubtedly held up for some years after they were patented, in 1912/1913, owing to wartime conditions. They were introduced into this country about the end of 1923 and at a still later date into the United States of America. Their use, however, has developed rapidly, both here and elsewhere, during the last few years. Their mechanical properties are admirably adapted for certain purposes and although experience has shown that, in so far as resistance to corrosion is concerned, they are very susceptible to certain forms of heat treatment and are not nearly so " foolproof " in their response to various manipulative processes as was at first imagined, they possess a very wide sphere of usefulness.

Neither these austenitic alloys nor the hardenable steels of either high or low chromium content represent, however, the whole of the metallurgist's endeavour to ·meet the engineer's demands for steels to resist corrosion. The last few years have seen great activity in the development of new types of stainless materials. Numbers of patents have been claimed and not a few steels put on the market. At the same time, many new uses have been found for the steels and one may specially mention in this respect, that product of the last decade—" heat-resisting " steel—which is frequently required to resist not only oxidation by air or by the products of combustion of ordinary fuels at high temperatures, but also the attack of corrosive gases, and in addition to possess considerable strength while so heated.

Broadly speaking, the developments as regards composition have proceeded along three main directions.

(1). The use of very high chromium contents, e.g., 25 per cent. or more, with or without sufficient nickel to make them austenitic. It should be noted that the use of such high chromium steels had been visualised in both the Krupp and the Elwood Haynes patents, but practical use only appears to have been made of them during the last few years.

(2). The addition of larger amounts of nickel than are found in the austenitic steels of the Krupp type. Thus the Société Anonyme de Commentry, Fourchambault et Decaseville took out, in 1917 and 1918, a series of patents for a group of steels - known collectively as " A.T.V." —in which the chromium content may vary from 10 to 15 per cent. and the nickel from 20 to 40 per cent. or even higher. Additions of a number of other alloys could also be made to these steels. Some three or four years later, C. M. Johnson obtained patents in the U.S.A. for steels containing somewhat similar amounts of chromium and nickel to those in the " A.T.V." series of steels and in addition 1/10 per cent. silicon.

(3). The addition of other metals—cobalt, copper, molybdenum, silicon, tungsten—either to the plain chromium steels or to one or other of the austenitic chromium nickel alloys. Many of these alloys are more or less in the experimental stage and few have been used to any great extent commercially.

As a result of all these numerous patents and developments, the metallurgy of steels resistant to corrosion has become rather complex, though in actual practice, some of the complexity is not so apparent, because most of the highly alloyed steels are much more expensive and more difficult to work than the simpler chromium and chromium-nickel steels and hence are only used, or recommended for use, when the corrosive conditions encountered are such that a reasonable life cannot be obtained from the simpler steels. An attempt is made, however, in the following pages to deal in a more or less systematic manner with the properties of the various types of these steels and finally to give some account of their present and possible uses.

THE INFLUENCE OF CHROMIUM ON THE STRUCTURE AND HARDNESS OF STEEL

CHAPTER II

The development of the science of metallography during
the past thirty years or so has enabled metallurgists not
only to evolve improved methods for the manufacture and
treatment of steel but also to give a logical explanation of
many of the practices which had been previously evolved in
a purely empirical manner by skilled craftsmen who have
built up so much of the art of steel making. (In the case of
alloy steels, the study of the structure and constitution of the
steel and the influence of the progressive addition of the
alloying elements on this structure and constitution has been
of fundamental importance both in the development of the
steels themselves and also of the heat-treatment most likely
to bring out the special characteristics of the several steels)
It is well known that the properties of ordinary steel can be
varied over a wide range by varying the composition of the
steel, mainly, of course, with regard to carbon, and also
that the properties of any given steel can be altered by
subjecting it to various treatments, either mechanical or
thermal or both combined. In addition to affecting the
physical properties, such as hardness, toughness, ductility,
etc., of the metal, these varying compositions and treatments
leave their mark on its structure, so that it has been one of
the aims of the metallurgist to follow these changes in the
structure and correlate them with the corresponding changes
in the physical properties.

The early development of some of the alloy steels
occurred at a time when metallographical investigation had
not attained the prominence which it now holds in the iron
and steel industry and when the fundamental principles
underlying the correct heat treatment of steel were not
appreciated or even understood. As a consequence, such
alloy steels as were used were, more often than not, employed

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in a condition in which their useful properties were not by any means fully developed ; owing to this, more expensive steels were used to obtain desired properties than were actually necessary. In the light of modern knowledge, some of the older investigations on such alloy steels and the accounts of the heat treatment suggested for these, form very curious though interesting reading.

In the case of stainless steel, knowledge of the changes produced in the internal structure of the metal by varying composition and treatment is of exceptional importance, because, in this case, not only do the ordinarily observed physical properties vary with such changes, but also the degree of resistance to corrosion. In order that the most efficient use may be made of stainless steel, the effects of such changes in composition and treatment must be thoroughly appreciated. Hence, a knowledge of the changes produced in the structure and constitution of the steel by different thermal and mechanical treatments and of the fundamental principles which underlie the metallographical explanation of these changes is very helpful not only to the manufacturer but also to the user of the steels. For this reason the author makes no excuse for dwelling at some length on the metallographical aspect of the subject. He believes that a general acquaintance with this aspect will be of great assistance to those who wish to take advantage of the almost unique properties of the steel and in order that it may appeal to those whose knowledge of modern metallography is limited, he has endeavoured to write in the simplest terms.

It will be gathered from what has been stated in the previous chapter that the fundamental constituent of all stainless steels is chromium. A very large proportion of the corrosion-resisting steel made to-day consists of plain chromium steels or irons. The more complex types may have their properties modified by the presence of small or large amounts of other metals, but in all of them, chromium is the dominating constituent. Without it, these complex alloys would hardly justify the name of corrosion-resisting steels. It is therefore logical, and it is also convenient, to consider first the simple chromium steels and afterwards the modifications and improvements produced by the addition of other metals to these chromium steels.

The addition of large amounts of chromium to steel

Plate 1

Fig. 1. Pearlite (dark) and ferrite (light) in ordinary steel containing 0·3 per cent. carbon. × 100.

Fig. 2 Laminated structure of pearlite 1,500 Photograph taken from annealed stainless steel but also typical of pearlite in ordinary steel
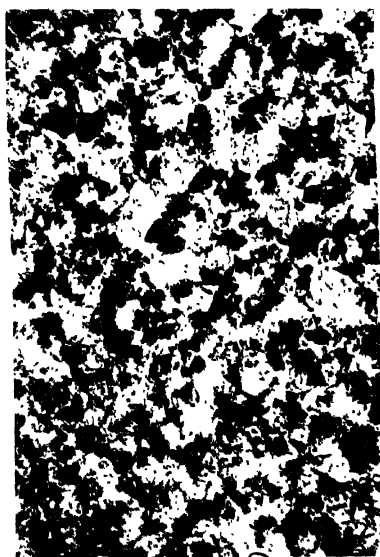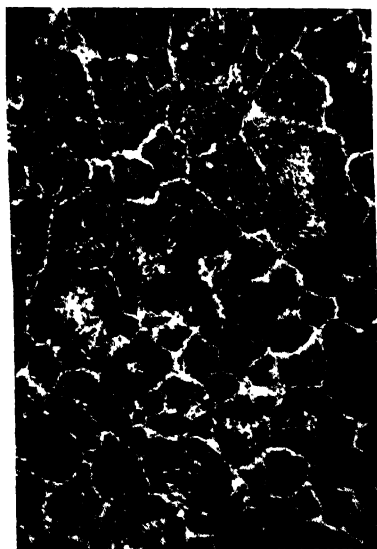

Fig. 3. Annealed stainless steel containing 0·15 per cent. carbon. × 100.

Fig. 4. Annealed stainless steel containing 0·5 per cent. carbon. × 300.
(Note network of free carbide.)

produces a number of characteristic effects on the properties
of this metal. Of these effects the four following are of
particular interest from the point of view of structural
characteristics and heat treatment. The presence of
chromium in steel :

(a) Lowers the carbon content of the micro-structural
constituent pearlite.

(b) Raises the temperature at which the carbon change
point occurs and hence the minimum tempera-
ture to which the steel must be heated before
it can be hardened by quenching.

(c) Diminishes very markedly the speed at which
carbon diffuses through the heated steel.

(d) Induces in the steel the property of air hardening,
that is, of hardening on air cooling from tem-
peratures above the carbon change point.

The influence exerted by these changes is fundamental.
The microstructures of ordinary carbon steels containing less
than 0·9 per cent. carbon are known to consist of mixtures
in varying proportion of two constituents, ferrite and pearlite.
The former consists of practically pure iron, hence its name,
while the latter is itself a mixture of iron and iron carbide,
arranged alternately in the form of thin plates. These
structural characteristics are now known to many users of
steel but, as a reminder and also as a standard with which
to compare the structures found in stainless steels, they are
typified in Figs. 1 and 2, the former representing the
appearance of an ordinary mild steel containing 0·8 per cent.
carbon when examined at a magnification of 100 diameters,
and the latter, the fine plate-like structure of pearlite, as
seen at the highest powers of the microscope.

Experiment has shown that the iron and carbide of
iron forming the pearlite are in such proportion that this
constituent contains 0·9 per cent. carbon, hence it follows,
because the ferrite contains no carbon, that in steels con-
taining less than 0·9 per cent. carbon, the amount of pearlite
increases proportionally to the carbon content from nil in
carbon-free iron to 100 per cent. in steel with 0·9 per cent.
carbon. Evidence of this is at hand in Fig. 1, in which the
area occupied by the pearlite is approximately one-third of

the whole. Increasing the carbon above 0·9 per cent. at which the whole mass consists of pearlite, leads to the formation of a third constituent, cementite or free carbide of iron, which may exist as a network round the grains of pearlite, similar to that shown in Fig. 4, as plates cutting across them or as more or less rounded particles.
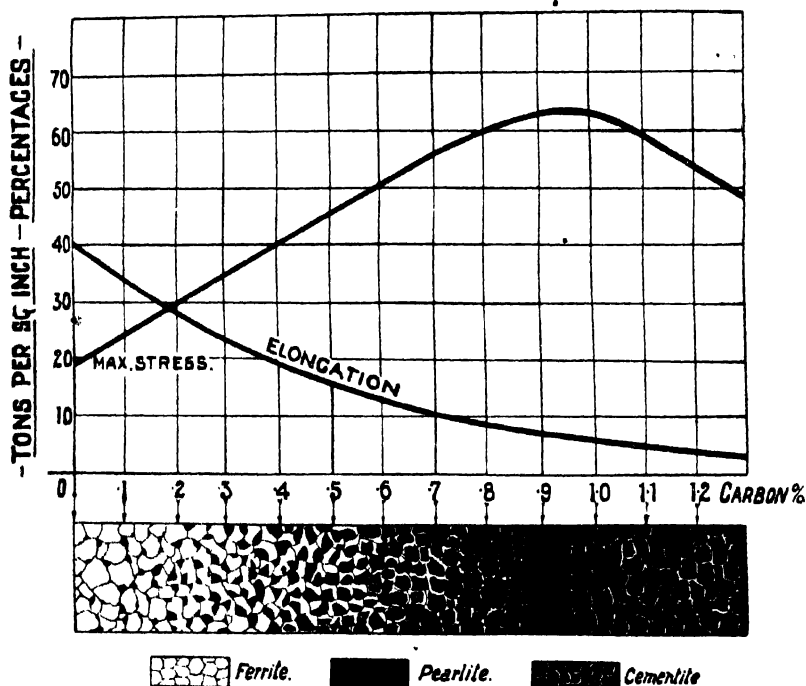
FIG. 5.   Influence of carbon on the structure and mechanical properties of ordinary carbon steels.

From this summary of the structural characteristics of ordinary carbon steels and from the known properties of pure iron, a soft ductile metal, and of carbide of iron, a hard brittle compound, one can readily understand that the mechanical properties of steels containing up to 0·9 per cent. carbon are approximately a linear function of the carbon content. Thus the tensile strength increases from about 18 tons per square inch in iron free from carbon to about 60 tons per square inch at 0·9 per cent. carbon, while at the same time the ductility, as represented by the elongation per cent. in a tensile test, gradually falls.

With more than 0·9 per cent. carbon, the physical characteristics of the carbide of iron impress themselves in a more marked manner on the properties of the resulting steel. Up to this percentage of carbon, the carbide of iron has existed solely as part of the constituent pearlite, with the result that the lack of ductility of the carbide has been to a great extent masked, because in pearlite each thin plate of carbide is sandwiched between two thicker plates of very ductile iron. The carbide existing free as cementite, however, is not subject to this moderating influence of ductile iron, hence it is not surprising to find that not only does the ductility continue to fall off as the carbon increases above 0·9 per cent., but in addition, the tensile strength begins to decrease as soon as the cementite is present in a sufficient amount to make its properties and structural condition felt. This brief analysis of the effect of increasing carbon content on the properties of ordinary steels is summarised in Fig. 5, which also shows diagrammatically the gradual change in structure with increasing content of carbon.

It will be apparent from the brief resumé given above that the factor which really governs the relation between the carbon content of steel and its mechanical properties is the amount of pearlite which can be formed from each carbon unit in the steel ; and this in turn depends on the carbon content of the constituent pearlite. As is indicated in Fig. 5, the addition of each 0·1 per cent. carbon, up to 0·9 per cent. increases the volume of the pearlite in the steel by one-ninth of the whole, due, of course, to the fact that this pearlite contains 0·9 per cent. carbon. If by any means, as for example the addition of alloys, the composition of this constituent is altered, then obviously the relation between the carbon content of the steel and its structure and properties will also be changed. In considering the influence on steel of any alloying metal, it is, therefore, of the greatest importance that its effect on the carbon content of pearlite should be known, because it is this value which determines to a large extent the useful range of carbon content available in the particular alloy steel. Actually it is found that chromium has a very considerable influence on this carbon value.

In a paper published in 1920, the author* described

* " The Structure of Some Chromium Steels." *J.I.S.I.*, 1920, I, 493.

some experiments for determining the composition of the pearlite in a series of chromium steels.   In these experiments ·use was made of cemented bars of low carbon steel containing different amounts of chromium. · The bars (which were one inch diameter and six inches long) were cemented for 24 to 36 hours at 1,000° to 1,100° C., so as to obtain a deep case ; they were then slowly cooled after cementing, in order that the bars should be in the pearlitic condition.
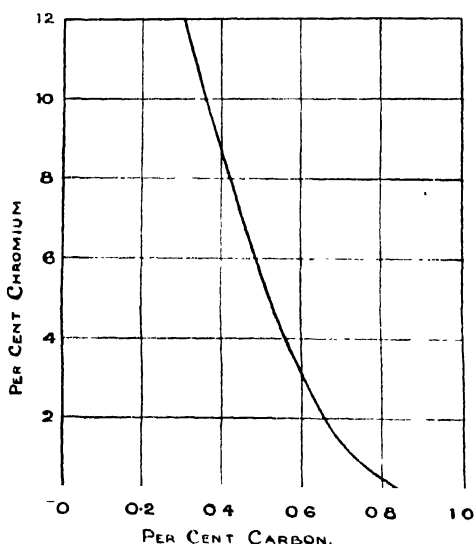
FIG. 6. Effect of chromium on the carbon content of pearlite.

After cleaning with emery, the bars were turned down, over half their length, in cuts 0·25 millimetre thick and each cut analysed for carbon.   From the remaining half of the bar, transverse sections were cut which were used for determining, microscopically, the depth to which free cementite existed in the bar.   From the results obtained the relationship between the carbon content of the pearlite and the amount of chromium in the steel was plotted in a curve which is reproduced in Fig. 6.   From this it will be seen that, in steel with 12 per cent. chromium, the pearlite contains slightly more than 0·3 per cent. carbon instead of 0·9 per cent., as found in steels free from chromium.   It will be evident, therefore, that carbon has a much greater effect in producing " steel " from iron with a high chromium content than from iron free from this alloying metal, and also that the useful

range of carbon content of such high chromium material
is likely to be much more restricted than in chromium-free
steels. As an instance of this, it may be pointed out that,
from a structural point of view, annealed material containing
12 per cent. chromium and 0·5 per cent. carbon, contains
a large amount of free carbide and corresponds in that
respect to a tool steel containing 1·3 to 1·5 per cent. carbon.

This will be evident from a glance at Fig. 4 which shows
the prominently visible network of free carbide existing in
steel containing the above-mentioned amounts of carbon and
chromium. In the same way, the grains of the pearlite in
Fig. 3, representing a stainless steel containing 0·15 per cent.
carbon, occupy almost half the area of the field and not
about one-sixth of it as would be the case with an ordinary
carbon steel containing this amount of carbon. The areas
of pearlite in both these samples had a structure similar to
Fig. 2, when examined at very high magnifications. This
typical photograph of pearlite was actually taken from a
sample of stainless steel. All the photographs shown in
Figs. 2 to 4 were taken from samples which had been very
slowly cooled from a high temperature, such a treatment,
as will be seen later, being necessary to obtain a pearlitic
structure in high chromium steel.

It is necessary to emphasise this effect of chromium
on the carbon content of pearlite. Experience of various
types of ordinary steels during a considerable number of
years has familiarised those dealing with steel with the
carbon contents most suitable for specific purposes. Thus
case-hardening steels contain, in general, 0·1 to 0·2 per
cent. carbon, axles and mild steel forgings, 0·25 to 0·35 per
cent., while in special forgings the percentage may rise to
0·40 or 0·45. Rails have a still higher carbon content, while
railway and tramway tyres may contain up to 0·75 to 0·80
per cent. Tool steels may contain still more carbon and to an
amount varying with the purpose for which they are intended.
Because this grading has been evolved in a more or less
empirical manner from the observed properties of steel, it is
perhaps not generally realised that it depends solely on the
carbon content of the eutectoid pearlite. The fact is
emphasised, however, in dealing with material such as
stainless steel, the pearlite of which has a very much smaller
carbon content. Owing to this marked difference, ideas as

to the carbon content most suitable for definite purposes, and evolved from usage with ordinary carbon steels, have to be completely modified in dealing with stainless steels.

It is well known that in ordinary pure iron or mild steel there is very great difficulty in introducing more than about 1·8 per cent. carbon even by prolonged cementation. As illustrated by the cementing experiments mentioned earlier, it is interesting to note the very high content of carbon which can be introduced into steels containing large amounts of chromium. In these experiments, the steels with a chromium content in the range used for stainless material were cemented for 36 hours at about 1,100° C. ; the outer layers of the bars thus treated contained approximately 3·0 per cent. carbon, while penetration had taken place to a depth of about three-eighths of an inch. These highly-carburised layers contained, of course, very large quantities of free carbide.

Changes in Structure Occurring on Heating and Cooling. Passing on to consider the further effects of chromium as set out in paragraphs (b), (c), and (d), page 33, all of which have a considerable bearing on the heat treatment of steel, it may be advantageous to recall briefly the effect of heat treatment on the structure and properties of ordinary carbon steels.

If a sample of ordinary mild steel, containing about 0·3 per cent. carbon, is gradually heated, no appreciable change is produced in its structure until a temperature of about 740° C. is reached. Similarly, quenching samples of the steel from any temperature below this value produces no appreciable change in the properties of the material. At about 740° C., the carbon change point generally referred to as Ac.1 occurs, being accompanied, as is well known, by a marked absorption of heat. During this change, the pearlite in the steel changes from a mixture of two separate materials, iron and carbide of iron, into a homogeneous solid solution which, for convenience, is called austenite. If a small sample of the mild steel be rapidly quenched in water immediately after this change has taken place, it will be found that the original structure of ferrite and pearlite has been replaced by another having the same general pattern as before but in which the pearlite areas are now occupied by a substance which shows no signs of the duplex

structure of the pearlite. This new constituent is called martensite and to it is due the hardness of quenched steel.

It will be noted that the areas occupied by the martensite in the quenched sample correspond to those which, when existing in the hot steel immediately before quenching, are referred to as austenite. The advisability of using different names for what appear at first sight to be two conditions of the same substance will be discussed later. Actually, it is found that there are important differences between austenite and martensite.

If the heating of the mild steel is continued, the solid solution, austenite, gradually dissolves the surrounding ferrite as the temperature rises until, finally, the whole mass consists of austenite. If small samples be rapidly quenched from a series of gradually increasing temperatures above 740° C., it will be found that the amount of the constituent martensite in these quenched samples gradually increases while that of the ferrite gradually gets less until, finally, the whole mass consists of martensite.

In the same way, if ordinary steel containing more than 0·9 per cent. carbon be heated, a similar series of changes takes place ; the pearlite is first replaced, at the Ac.1 change, by austenite which then, as the temperature rises, gradually dissolves the cementite.

Although martensite does not possess the duplex structure of pearlite it shows, on more or less deep etching, a characteristic structural appearance which suggests a series of interlacing needles. This appearance, which is illustrated in Fig. 11, is connected with the crystalline structure of the martensite or of the austenite from which it was formed. The size and distinctness of this structural pattern increase markedly as the temperature of quenching is raised above that of the Ac.1 point.

It would be expected that the temperature required to produce, on heating, a homogeneous mass of austenite in any particular steel, will vary with the amount of ferrite or cementite which it contains ; this is actually the case and the results of numerous experiments in this direction are summarised in the diagram shown in Fig. 7. This shows, again as would be expected, because it affects only the constituent pearlite common to all steels, that the carbon change point, on heating, occurs at sensibly the same temperature

for any carbon content, a fact indicated by the 'continuous line, Ac.1* running across the diagram at 740° C. The tempera-
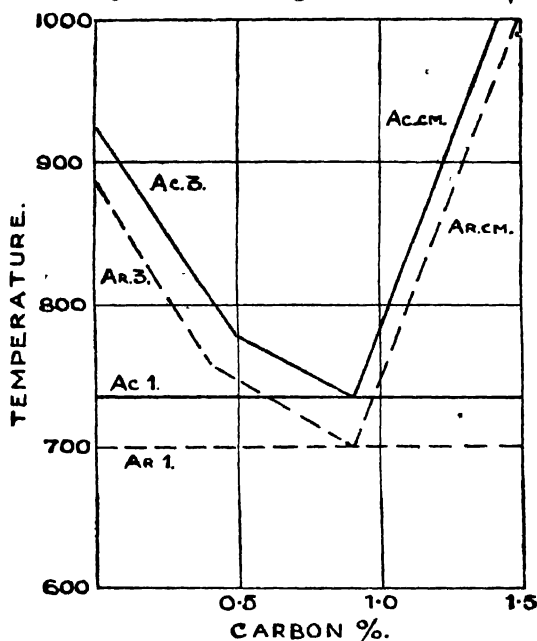
Fig. 7.   Effect of carbon content on the critical changes occurring on heating and cooling ordinary steels.

ture of final solution of the ferrite is marked by the line Ac.3, which falls from about 920°C. in practically carbonless material to 740°C. at 0·9 per cent. carbon, where it joins the Ac.1 line.   In the same way, the line Ac.cm. represents the temperature of complete solution of the cementite and this will be observed to rise very rapidly as the amount of carbon increases above 0·9 per cent.

On slowly cooling the steels, the corresponding changes take place in the reverse order, but at temperatures approximately 50° C. below those at which they occurred on heating. Thus the dotted lines Ar.3 and Ar.cm. mark the beginning of the separation of ferrite and of cementite respectively while Ar.1 similarly marks the change of austenite back into pearlite.

From what has been said it will be evident that, of all

* The use of the "shorthand sign" *Ac.1* is readily understood when it is remembered that these letters are an abbreviation for the French words *arrêt* (arrest), *chauffage* (heating).   The numeral 1 distinguishes this point from others which occur at other temperatures on heating: Similarly changes on cooling are indicated by the letters *Ar*, the second letter indicating *refroidissement* (cooling).

Plate II

Fig. 8. Slowly cooled from a high temperature producing a pearlitic structure

Fig. 9. Sample similar to Fig 8 reheated to 825 C, and quenched in water.

Fig. 10. As Fig 9, but reheated to and quenched from 950 C.

Fig 11. As Fig. 9, but reheated to and quenched from 1050 C

FIGS 8, 9, 10, 11. STAINLESS STEEL CONTAINING 0·3 PER CENT CARBON
AND 12 PER CENT. CHROMIUM AFTER VARIOUS TREATMENTS.
All magnified 750 diameters.

carbon steels, the simplest, from the point of view of changes occurring during heat treatment, is one containing 0·9 per cent. carbon. 'Such a steel normally consists solely of pearlite ; on heating it has one change point, at 740° C., at which the pearlite changes to austenite. A small sample rapidly quenched from any temperature above this consists entirely of martensite. A steel of this composition is frequently called·" eutectoid," a term which has been coined, from Greek words, to indicate that the structural changes, which occur in such a steel on heating, are completed at a lower temperature than in steel of any other carbon content. This, of course, is evident from the diagram Fig. 7. Steels which contain less carbon than 0·9 per cent. are termed hypoeutectoid, and those with higher carbon hypereutectoid.

If any confidence may be placed in analogy it would be expected that, in stainless steels, the simplest changes on heating and cooling will be found also in steel of eutectoid composition and actually it is found that the changes in structure and properties occurring in stainless steels are much more readily understandable if attention is first given to steel of such composition. It will also be an advantage if at the outset steels containing about 12 per cent. chromium are considered.

One of the effects of the presence of large amounts of chromium in steel, as noted on page 33, is that the steel acquires the property of hardening when cooled in the air from temperatures above the carbon change point. Owing to this property, to which more detailed consideration will be given later, it is necessary to cool stainless steel very slowly from a fairly high temperature in order to produce in it a pearlitic structure. However, a steel containing about 12 per cent. chromium and 0·30 per cent. carbon, i.e., of eutectoid composition, slowly cooled from a temperature of 1,000° C. or over, consists of well-defined pearlite, as shown in Figs. 2 and 8, and has a Brinell number of about 200. If small samples of such a steel are quenched from a series of gradually increasing temperatures, it will be found that no change in the structure or the hardness of the quenched piece is produced until a temperature of about 800° C. is reached, owing to the fact, stated in paragraph (b), page 33, that chromium raises the temperature at which the carbon change point occurs. Here the Ac.1 change occurs and, as in ordinary steels, is accompanied by a well-defined absorption of heat.

Whereas, however, in ordinary carbon steels the solution of the carbide in the pearlite takes place very rapidly at the Ac.1 point, in stainless steels, as in all high chromium steels, it takes place much more slowly. As a result of this, the absorption of heat in these steels, which is generally referred to as Ac.1, is actually only the commencement of this change because only part of the eutectoid carbide dissolves at that temperature, the remainder going progressively into solution as the temperature rises over a range of 150°/200° C. above this point. For convenience, however, the temperature marking the heat absorption at the beginning of this range will be referred to in the following pages as the Ac.1 change. If two small samples of the steel in question are quenched, one immediately below and the other immediately above this Ac.1 point, it will be found that the latter is considerably harder than the former and, when prepared as a microsection, etches more slowly, but the microstructures of the two appear to be almost identical. In that quenched below the change point, the structure consists of pearlite, or fine lamellae of carbide more or less evenly distributed through a ground mass of ferrite, precisely similar to Fig. 8 ; that quenched above the change consists of lamellae of carbide, less in number than before but similarly distributed in a background of martensite. Owing, however, to the lamellae of carbide being closely packed, the background has little chance to develop any· distinctive signs of martensitic structure. The similarity between the structures of two such samples as these is illustrated by comparing Figs. 8 and 9, the latter representing a sample quenched from 825° C., i.e., about 25° or so above Ac.1. The resemblance between the two structures is evident, as is also the large amount of carbide remaining undissolved in the sample quenched from 825° C.*

* Probably the most convenient etching reagent for these steels is a 10 per cent. solution of hydrochloric acid in alcohol ; the time of etching with this reagent varies according to the condition of the steel, being approximately three to five minutes for annealed samples and twenty to thirty minutes for those which have been hardened. For use with higher chromium steels, especially those of low carbon content, the strength of the hydrochloric acid solution may be conveniently increased to 15 per cent., and 5 per cent. nitric acid added.

‡ In order to show the carbide in stainless steels, the reagent proposed by Murakami is also very useful. This reagent (an aqueous solution containing 10 per cent. of caustic potash and 10 per cent. of potassium ferricyanide) darkens the carbides, leaving the other constituents unaffected and has, therefore, an action similar to that of sodium picrate on ordinary steel. It may be used cold, in which case about 10 or 20 minutes' attack may be required, or boiling, when the attack is more rapid.

' As the temperature rises above the Ac.1 point, the amount of carbide remaining undissolved becomes less and less, while in samples quenched from a series of gradually increasing temperatures, the appearance of martensite becomes more pronounced. Finally, at a temperature of about 1,000° C., depending to some extent on the rate of heating, the time of soaking at the maximum temperature and also on the chromium content, complete solution of the carbide is obtained ; samples quenched, or air cooled, from this temperature or above consist of martensite —see Figs. 10 and 11.

As a consequence of the gradual solution of the carbide above the Ac.1 change point, stainless steel does not attain its full hardness on quenching immediately above this point ; on the contrary, the hardness of quenched samples increases as the quenching temperature is raised through the range of 150°/200° C. above this point during which, as previously described, the carbide is gradually dissolving. This is shown in Fig. 12, which represents the Brinell hardness numbers obtained from a series of samples quenched at gradually increasing temperatures.

Having traced the changes occurring on heating a sample of stainless steel to the point at which it becomes fully hardened when quenched, the structure so produced consisting entirely of martensite, attention may next be given to the effect produced by tempering such a sample. If a fully-hardened sample of ordinary carbon steel of eutectoid composition be reheated to a series of gradually increasing temperatures, it is well known that the hardness of the steel is gradually reduced.

Fig. 12. Brinell hardness number obtained from annealed stainless steel (0·30 per cent. carbon) after water quenching from the temperatures indicated.

After tempering up to about 200° C., there is practically no loss of hardness, but as the temperature rises above this figure up

to 740°C., the Ac.1 point, the hardness falls almost uniformly. This is indicated in curve B in Fig. 13, which shows the Brinell hardness numbers obtained on tempering such a steel at a series of gradually increasing temperatures. From each tempering heat the sample was quenched in water, hence the Ac.1 point which occurred at 740 C. is marked by a sudden increase in the hardness.   On tempering in the same manner a hardened sample of stainless steel, changes similar to those occurring in the ordinary carbon steel are produced but they occur at much higher temperatures.
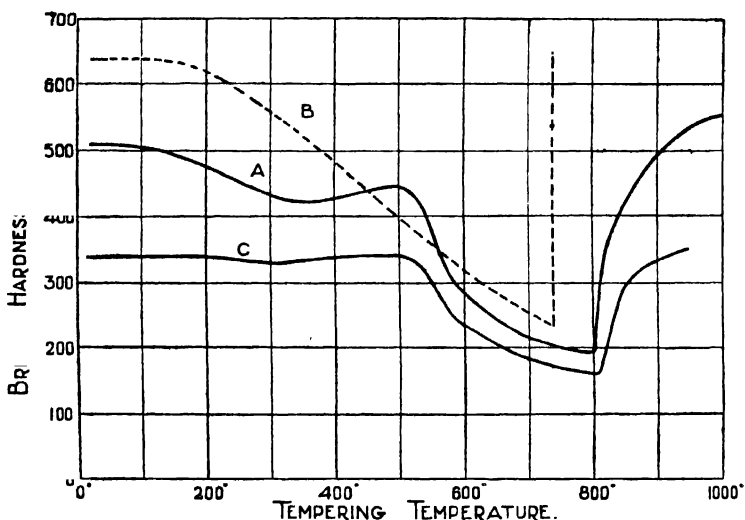
Fig. 13.   Brinell hardness numbers obtained on tempering hardened steels at gradually increasing temperatures, the samples being water quenched from each tempering heat.   ·

A.   Stainless Steel   (0·30 per cent carbon).
B.   Carbon Steel   (0·90 per cent. carbon).
C.   Stainless Iron   (0·07 per cent. carbon).

With the high chromium steel, the hardness remains almost unchanged up to 500° C. or slightly higher. At about 550° C. softening takes place rather suddenly, the hardness falling rapidly so that by the time the temperature has reached 600° C. the Brinell hardness number has a value of 250 to 300.   From 600° C. up to 750° or 800°C., the hardness falls slowly and steadily to a value of about 200 Brinell.   In curve A, Fig. 13, are plotted the Brinell hardness numbers obtained on tempering such a steel at

Plate III

Fig. 14. Hardened and then tempered at 700° C. Brinell 207. 1,000
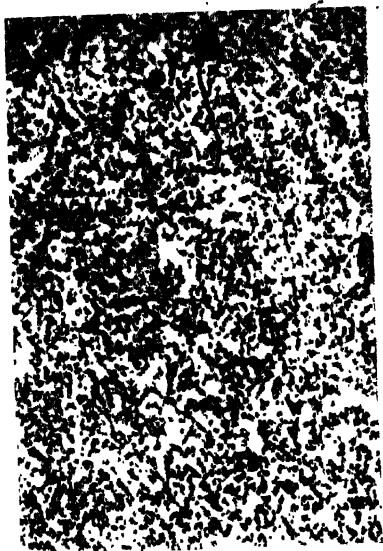
Fig. 15. Oil hardened 900° C. Brinell 437. 1,000

Fig. 16. Martensite (light) and troostite (dark) in sample moderately slowly cooled from 1,200° C. Brinell 364. 250.
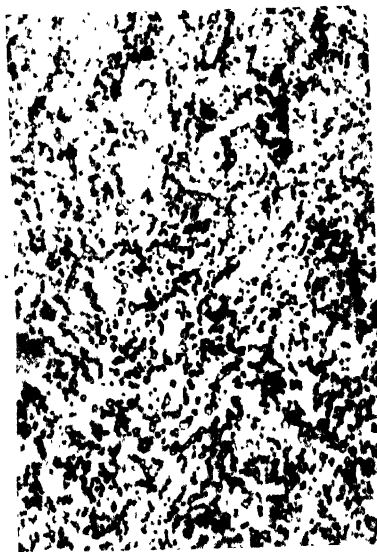
Fig. 17. Annealed 860° C. Brinell 170. 1,000.

FIGS. 14, 15, 16, 17. STAINLESS STEEL: 0·30 PER CENT. CARBON, AND 12 PER CENT. CHROMIUM.

gradually increasing temperatures and a comparison of this with curve B in the same diagram indicates clearly the differences between the two types of steel. Curve A also shows very plainly the three ranges of tempering temperature, mentioned above, which occur in the tempering of stainless steel. From a practical point of view, the third range, from about 600°, to 750° or 800° C. is very interesting and useful, because a steel which on tempering does not alter very much in hardness or tensile strength over a range of fifty or a hundred degrees of tempering temperature is obviously more easy to heat treat on an industrial scale than one in which the hardness changes rapidly as the temperature increases. On the other hand, the very sudden fall in hardness occurring between 500° and 600° C makes it difficult to secure prescribed properties by tempering stainless steel in this range.

The alterations in hardness occurring on tempering a hardened sample of stainless steel are accompanied by changes in the structure of the steel. After tempering at temperatures up to 500° C., in the range in which the hardness remains practically constant, the structure still consists of martensite similar to that in the untempered sample, though it probably requires a shorter attack than the latter by the etching fluid to develop its structure. The sudden drop in hardness occurring between 500° and 600° C. is accompanied by a change in the structure, the martensite being replaced by sorbite, consisting of very fine particles of carbide, only visible at the highest powers of the microscope, embedded in a ground mass of ferrite. In the third range of tempering, between 600° and 700° or 800° C., the particles of carbide, which have separated out previously, gradually coalesce into larger globules. Such a fully tempered sample has therefore the structure shown in Fig. 14.

If the heating of the hardened and tempered sample is continued to still higher temperatures, the same sequence of events as was described on page 42, takes place again. The Ac.1 point occurs at about 800° C., austenite is again formed, part of the carbide goes into solution while the remainder gradually dissolves as the temperature rises above this point. Similarly the hardness of quenched samples increases with increase in quenching temperature as indicated in the right hand part of curve A in Fig. 13. The

structure of such a sample quenched at 900° C. is shown in Fig. 15, and this may be regarded as typical. of the normal structure of hardened stainless steel.

Effect of Rate of Cooling on Hardness and Micro-structure. Several references have already been made to the effect of comparatively large amounts of chromium in inducing in steel the property of air hardening. It may be advantageous to consider this in a little more detail. It is a matter of general knowledge that if a piece of ordinary carbon tool steel is rapidly quenched in water from a suitable temperature, it is hardened. If quenched from the same temperature in oil, or other medium giving a slower rate of cooling than water, it is less hard while if cooled at the still slower rate obtained by allowing a small sample to cool freely in the air, it is much softer. These results suggest that there is a distinct connection between the rate of cooling of a sample and the degree of hardness produced in it, and also that in order to harden ordinary carbon steel a very rapid rate of cooling is necessary. That this is the case is familiar to the smith, who knows that if he quenches in water, from a good hardening temperature, a piece of carbon tool steel in the form of a bar about half an inch in diameter, it will be hardened throughout and will break with a fine even fracture. If, however, he similarly quenches from the same temperature a larger sized bar, e.g., one and a half inches in diameter, of the same steel, this will not harden to the centre but in breaking will show a soft core.

If the hardening experiment, using the different rates of cooling given by water, oil and air quenching, be repeated with a steel containing the same amount of carbon as before and in addition 1·5 or 2 per cent. of chromium, it will be found that, although the bar cooled in air is comparatively soft, both the one quenched in oil and that quenched in water are as hard as the water-quenched bar of ordinary carbon steel. This suggests that the presence of the chromium has allowed the steel to harden at a slower rate of cooling. Chromium has this action and to an extent which increases with the amount of this element present, so that with such a high percentage of chromium as is contained in stainless steel, the changes which should occur on cooling the steel from a hardening heat are retarded to such an extent that the steel hardens

when air-cooled from such a temperature. The hardness
so produced in stainless steels, however, is not independent
of the rate of cooling ; variations in this rate effect similar
changes to those produced by different rates of cooling in
ordinary steels, but the actual values of the rates necessary
to give similar effects in the two types of steel are widely
different. As with ordinary steel, so with stainless steel,
there is a fairly definite rate of cooling which must be
exceeded to bring about hardening. This rate, however,
varies with the composition of the steel and also, in any given
steel, with the temperature from which it is cooled. The
higher this temperature is above the Ac.1 point, the slower
the rate at which the steel may be cooled and yet be hardened.
This is illustrated in Fig. 18, which represents the Brinell
hardness numbers obtained from samples of a stainless steel,
of approximately eutectoid composition, after being cooled
at different rates from 860° and 1,200° C., respectively, '
the rate of cooling being measured by the time taken to cool
over the range 850° to 550° C.* The curves in this diagram
show that, to obtain a Brinell hardness number of at least
400 in the steel tested, the cooling time should not exceed
about two minutes when cooled from 860° C., but may
reach 60 minutes when the maximum temperature is 1,200° C.
With slower rates of cooling than these, the steel becomes
progressively softer until the completely annealed condition
is obtained, in which state the steel corresponds to the
normalised condition of ordinary carbon steels. The
rates of cooling necessary to harden or to anneal any particular
steel depend on its carbon and chromium content, and are
also materially affected by the content of other elements
present, notably nickel. The rate at which a steel must be
cooled in order to anneal it completely is slower the higher
the chromium and nickel content ; on the other hand, high
carbon alloys are more easily annealed than those of lower

* The range 850° to 550° C. was adopted for taking the cooling rates in these
experiments largely from the point of view of convenience. Actually, however,
it is found by experiment that this interval of temperature includes practically
all the range in which the Ar.1 point in stainless steel takes place on slow cooling,
and that providing this range of temperature is passed through at the requisite
rate, the speed of cooling below 550° C, or in any case 500° C, does not materially
affect the hardness produced. To give some concrete idea of the meaning of the
rates of cooling given in Figure 18 it should be mentioned that a bar three-quarters
of an inch in diameter on cooling freely in the air occupies about 1½ minutes in
passing through the range 850° to 550° C, providing no evolution of heat occurs
in the sample itself.

carbon, but otherwise of similar composition, i.e., they anneal at faster rates of cooling.
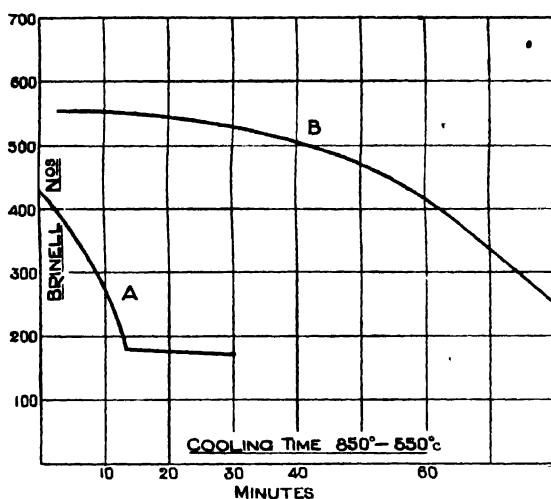
Fig 18.   Effect of varying rates of cooling on the Brinell hardness number of stainless steel when cooled from 860°C. (curve A) and 1,200°C. (curve B).

The actual microstructure obtained on annealing stainless steel also depends on the maximum temperature to which the steel was heated prior to the slow cooling. If this temperature was sufficiently high to dissolve all the carbide, a pearlitic structure, practically indistinguishable from that of ordinary carbon steel and similar to Figs. 2 and 8, is obtained on complete annealing. For the production of such a structure a very slow rate of cooling is necessary, as will be evident from Fig. 18. With rates of cooling from this temperature, intermediate between this and that necessary to harden the sample (that is, rates of cooling such as would give Brinell hardness numbers between 400 and 200, see Fig. 18), the structure consists of mixtures of martensite and finer or coarser forms of pearlite. The sequence of structural changes obtained in this range of cooling rates may best be illustrated by considering a rate of cooling just sufficient to harden the sample completely. As the cooling rate becomes gradually slower than this, the structure which, in the fully hardened sample, consisted entirely of martensite, now begins to show small areas which etch very rapidly and appear under the microscope

as black structureless masses. These areas are known as troostite; they consist of a mixture of iron and carbide of iron, similar to pearlite, but in which the separate particles are so small as to be indistinguishable separately at the highest powers of the microscope. As the rate of cooling becomes still slower, the amount of troostite increases, the hardness correspondingly decreasing, until the whole mass consists of this constituent, and then with still slower rates the particles of carbide and of iron in the troostite get coarser and coarser till, finally, well-developed laminated pearlite is obtained. The progression of structure from martensite to pearlite is therefore precisely similar to that obtained on varying the cooling rates for ordinary carbon steel, except that the rates for producing similar structures in the two steels are widely different. Fig. 16 shows a structure consisting of martensite and troostite ; the sample from which this was taken had a Brinell hardness number of 364.

If, however, the steel is cooled more or less slowly from temperatures above the Ac. 1 point but insufficiently high to dissolve all the carbide, the microstructures obtained differ from those described in the last paragraph. It has been shown on page 42 that when stainless steel is quenched from any temperature in this range, the structure consists of particles of carbide distributed in a ground mass of martensite (see Figs. 9, 10, and 15). With somewhat slower rates of cooling than that necessary to harden the steel from this range of temperature (that is, corresponding to about 5 to 12 minutes, curve A, Fig. 18), the background etches darker and the structure looks confused but no real appearance of troostite is produced, such as is obtained on cooling from high temperatures. Finally, with still slower rates of cooling one obtains a completely annealed material having a granular structure, such as is shown in Fig. 17, which is very similar to that produced by hardening and fully tempering the steel except that the grains of carbide are considerably larger in the annealed sample than in the other ; this will be evident on comparing Figs. 14 and 17.

It is possible, however, to obtain with these semi-annealed samples some interesting etching figures with the 5 per cent. solution of picric acid in alcohol which is generally used for the microscopical etching of samples of

ordinary steel. This reagent has practically no effect on sections of stainless steel which have been hardened or hardened and tempered. If, however, samples cooled at the intermediate rates described in the last paragraph are etched with picric acid an appearance of troostite is produced. Thus Fig. 19 shows at a medium magnification a sample cooled from 860° C. at a rate of 9 minutes, and having a Brinell hardness number of 245, after etching with picric acid; the appearance strongly suggests a mixture of martensite and troostite. If, however, such samples are examined under the highest powers of the microscope it will be seen that the patches are not troostite but groups of carbide granules, as shown in Fig. 20. A probable explanation of the appearance shown in Fig. 19 is that the darker parts of the section are more readily attacked than the rest by the weak picric acid because they are the initial decomposition centres of the martensite.

If samples slowly cooled from high temperatures, and consisting of mixtures of martensite and troostite (e.g., similar to Fig. 16) are etched with picric acid, the troostite is distinctly etched while the martensite remains quite unattacked. If such a sample be subsequently tempered at about 700°C . (so as to give in the martensite areas a structure similar to Fig. 14) and then etched with picric acid, again only the troostite areas are etched. The areas having the hardened and tempered structure, which were formed from the martensite existing before tempering, remain quite white. These results with picric acid etching have an interesting bearing on the relative resistance to corrosion of annealed and hardened and tempered samples of the steel; they will be referred to later.

Influence of Carbon Content on Micro-structure. Having discussed the changes occurring in a stainless steel containing about 12 per cent. chromium and of approximately eutectoid composition, the influence of varying carbon content on such a steel may next be considered.

When annealed at high temperatures, 1,000° C. and upwards, steels with lower carbon content than eutectoid composition consist of mixtures of ferrite and pearlite similar to those of ordinary mild steels, except that there is a distinct tendency for the ferrite in the high chromium

Plate IV
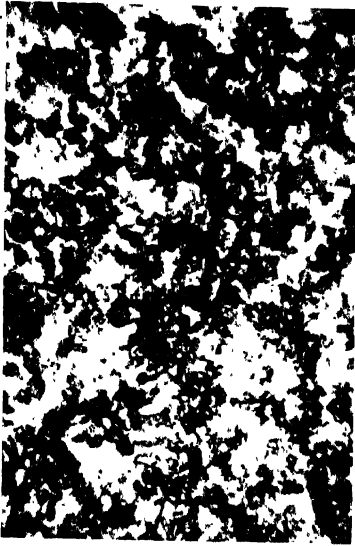
Fig. 19. Stainless steel, 0.4 per cent carbon, 12 per cent chromium, cooled from 860 C. at a rate not quite fast enough to harden it. Brinell 245. Etched with picric acid. ×250

Fig. 20. Dark part of Fig. 19. ×1,000
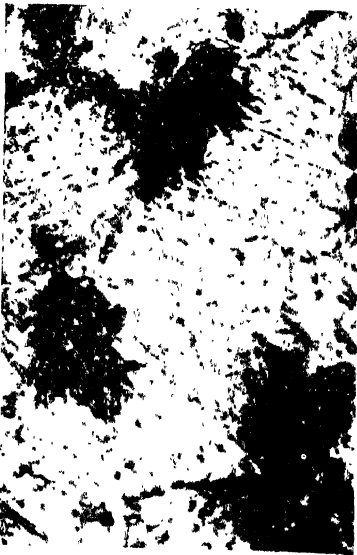
Fig. 21. Stainless steel, 0.15 per cent carbon, 13 per cent chromium, slowly cooled from 1,050 C. ×750
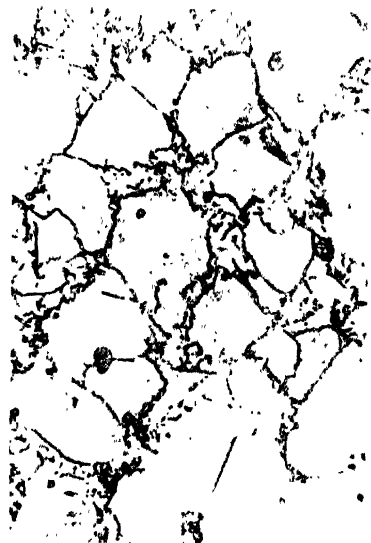
Fig. 22. Stainless iron, 0.07 per cent carbon, 13 per cent chromium, slowly cooled from 1,050 C. ×750

steels to contain isolated globules and laminae of carbide. This is illustrated in Fig. 21, which represents the structure of a steel with 0·15 per cent. carbon slowly cooled from 1,050° C. The carbide particles can also be seen in Fig. 3, which shows the same steel at a lower magnification. It will be noted that the pearlite areas in this sample occupy about half the field, as would be expected, because the carbon content of the steel is about half that of the pearlite in stainless steel. When the carbon is reduced to the limits generally found in stainless iron, 0·10 per cent. or less, the carbide in the pearlite tends to ball up so that such low carbon material, when annealed from high temperatures, often consists of ferrite grains with globules of carbide tending to form a network round them. A typical example is shown in Fig. 22. On the other hand, when such hypoeutectoid steels are air-cooled or quenched in water or oil from high temperatures, they consist entirely of martensite unless the carbon is very low, when free ferrite may also be present, more particularly in air-cooled samples. The presence or absence of ferrite is also materially influenced by the composition of the steel apart from chromium and carbon ; thus low carbon material containing comparatively large amounts of silicon is more likely to contain ferrite than a steel low in silicon but otherwise similar in analysis, when both are treated in the same way ; nickel acts in the opposite manner.

On tempering hardened samples of the low carbon alloys, the Brinell hardness number falls in a manner similar to that of the higher carbon steel, as shown in curve C, Fig. 13. On passing the carbon change point, the carbide in the pearlite also behaves in the same way as that in eutectoid steel ; that is, part of it dissolves at the actual absorption of heat and the remainder as the temperature rises above this. The temperature required for complete solution of the carbide under ordinary conditions of heating, e.g., soaking for 30 to 60 minutes at the maximum temperature, depends to some extent on the previous distribution of the carbide ; if the latter be evenly distributed, as occurs when a previously fully hardened sample, consisting entirely of martensite, is reheated, complete solution is obtained somewhat earlier than if the same steel had been previously annealed so as to give a structure of ferrite and pearlite. This difference is

understandable from the very slow rate of diffusion of the carbon in such high chromium steel, and the greater distance which the carbide has to diffuse in the case of the sample with the ferrite and pearlite structure. The persistence of the carbide particles may be illustrated by Fig. 23, which is taken from a small disc, six mm. thick, of steel, having initially the structure shown in Fig. 21, after reheating for one hour at 900° C., followed by quenching in water. Even in extremely mild steels, with 0·10 per cent. carbon or less, carbide may be detected in samples quenched 50° to 100° C. above the carbon change point.

The Ac.3 line for these steels, representing the temperature of the complete solution of the free ferrite on heating, has not yet been worked out ; its position appears to alter quite considerably with variations in the content of silicon, manganese and nickel, small but variable amounts of which are almost always found in stainless material. The ferrite, however, is gradually dissolved as the temperature rises above the Ac.1 point. Figs. 25 and 26 show the structure of small samples of steel containing 0·09 per cent. carbon and 12·3 per cent. chromium after quenching from 825° and 875°C., respectively, and illustrate the gradual solution of the ferrite. When quenched from still higher temperatures, the structure became entirely martensitic. Further structural changes in low carbon steels may take place at very high temperatures, e.g., 1300° C. and upwards ; these will be referred to later.

After hardening and then tempering between 600° and 750° C., low carbon alloys consist of ferrite with particles of carbide more or less evenly distributed—see Fig. 24. When annealed from temperatures just above the Ac.1 point, they consist of ferrite and rather coarse granules of carbide, similar to those in Fig. 17, but less in number, the distribution of the granules depending to some extent on the previous history of the sample.

Stainless steels of hypereutectoid composition behave in a manner analogous to ordinary high carbon steels. The excess carbide gradually dissolves after the eutectoid carbide has been taken into solution. In the paper previously referred to,* the author traced out the solubility line of the free carbide in a steel containing 11·2 per cent. chromium ;

* *J.I.S.I.*, 1920, I, p. 493.

Plate V

Fig 23 Material shown in Fig 21 after reheating to 900 C for one hour, and then quenching showing carbide remaining undissolved × 1,000

Fig 24 Stainless iron, 0.07 per cent carbon, 13.3 per cent chromium, hardened 950°C and tempered 700 C Brinell 174 × 1000
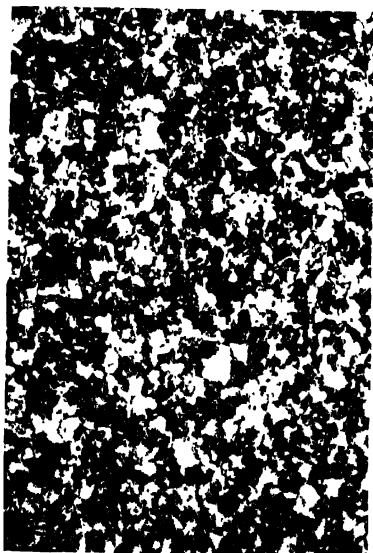
Fig 25 Stainless iron, 0.09 per cent carbon, 12.3% chromium, water quenched from 825 C Brinell 241 × 100
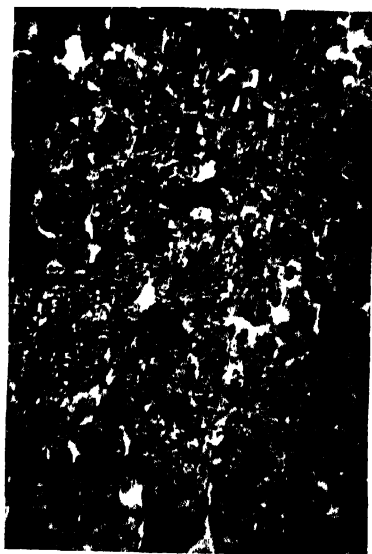
Fig 26 Same material as Fig 25 but quenched from 875 C Brinell 364 × 300

the results obtained are reproduced in Fig. 27, from which
it will be seen that in such a steel, the carbide corresponding
to 0·35 per cent. carbon, is dissolved at 1,000° C., to 0·45 per
cent. at 1,100° C. and to 0·9 per cent. at 1,200° C. As with
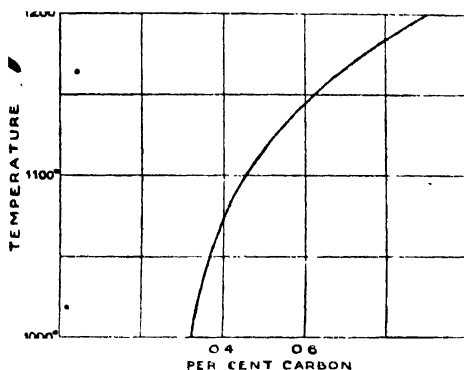
Fig 27.   Solubility of free carbide in stainless steel (11·2 per cent.
chromium) at high temperatures.

the solution of the eutectoid carbide, there is probably
a considerable " time element " in the solubility of the
excess carbide. The figures given refer to experiments in
which the samples were held at the indicated temperature
for half-an-hour.   With considerably longer periods of
soaking, the amounts of carbon dissolved at any temperature
would probably be somewhat greater.

Stainless Steels with High Carbon Content.   Steels
with about 12 per cent. chromium which have a relatively high
carbon content, e.g., 0·8 to 1 per cent., can perhaps hardly
be referred to as ordinary types of stainless steel because, as
will be seen later, their resistance to corrosion is considerably
less than that of steel with lower carbon content but otherwise
similar in analysis. They are, however, of considerable interest
theoretically and as their properties show in a somewhat
exaggerated form the effects, not always advantageous, of
using a higher carbon content than is normally present in
stainless steel, it may not be out of place to consider them
briefly.   Such steels contain very large amounts of free
carbide and as this is only taken completely into solution
at very high temperatures, if at all, their heat treatment,
especially as regards refining a coarse structure, presents

obvious difficulties. Owing to the presence of this large amount of carbide, they are not particularly soft even when fully tempered. Such high carbon steels are also very easily burnt, owing to the fact that they commence to melt at lower temperatures than many other steels ; however, the characteristic structure of such burnt steel, showing the presence of large amounts of partially melted material having a characteristic dotted eutectic structure as shown in Fig. 31, makes the diagnosing, in " post mortem " examinations, of the trouble arising from this, comparatively easy. These steels are also much harder to forge than the lower carbon steels and as the reheating temperature may not be raised unduly, owing to the danger of burning, the hot working of such steel is, therefore, much more difficult than that of the lower carbon steels.

From a theoretical point of view, however, their most interesting feature lies in the fact that when quenched from very high temperatures, 1,200° C. or thereabouts, they do not harden, owing to the fact that the austenite which exists at these high temperatures is retained as such on quenching and does not change into martensite. During the quenching of ordinary steels or of the lower carbon varieties of stainless steel, the changes which would normally occur at the Ar. 1 point during slower cooling are not entirely suppressed, though the separation of the carbide of iron and of the iron into microscopically visible particles is, of course, entirely prevented. The part of the change which still occurs, in spite of the utmost rapidity of quenching, concerns the iron itself. The power which the iron in the pearlite acquires, when heated to the Ac.1 point, of dissolving the alternate lamellae of carbide, is due to a rearrangement in its own crystalline structure. Carbon is almost completely insoluble in the ordinary form of iron existing at atmospheric temperatures, but with the change in its crystalline structure, which takes place when austenite is formed, iron acquires the power of dissolving a limited amount of carbon. There are other differences in the physical properties of the two forms of iron ; thus the ordinary low temperature variety, which for convenience is designated a-iron, is strongly magnetic, while the high temperature type, known as γ-iron, is practically non-magnetic. During the slow cooling of ordinary steel, or of stainless steel, the Ar.1 point

Plate VI

FIG. 28. Steel containing 1·01 per cent carbon and 11·8 per cent. chromium, hardened and fully tempered. Brinell 241. 1,000. (see page 58.)

FIG. 29. Same steel as Fig. 28 but quenched from 1,000 C. Brinell 627. 750. (see page 58.)

FIG. 30. Austenite obtained by quenching, from 1,200°C., steel with 0·67 per cent. carbon, and 14·1 per cent. chromium. 500. (see page 58.)

FIG. 31. Burnt sample of high carbon stainless steel showing characteristic eutectic structure. × 500.

marks the change of the γ-iron of the austenite to α-iron
with the coincident precipitation from solution of carbide
of iron. By rapidly quenching the stainless steels considered
up to now, the precipitation of the carbide is prevented but,
as with ordinary carbon steels, the change of the γ-iron to
α-iron cannot be suppressed and, under such conditions, this
part of the change takes place at about 300° C., leading to
the production of martensite, which incidentally is magnetic,
from the austenite. In pure iron the change from the
gamma form to the alpha occurs at about 900° C., and
in such material it is not possible, even by the most rapid
quenching, to prevent this change taking place. In the
presence of carbon, the γ-form containing this element
in solution remains stable down to the Ar.1 point at
about 700° C. on slow cooling and is retained to still lower
temperatures on quenching. The presence of chromium in
the steel lessens still further the tendency of the γ-iron to
change to the α-form on cooling, so that when both chromium
and carbon are present in sufficient amounts in solution in
the iron, the stability of the γ-form is increased to such an
extent that it may be preserved unchanged during cooling to
ordinary temperatures. Other alloying metals, e.g., nickel
and manganese, have similar effects on the structural changes
occurring in steel and hence, when present in sufficient
amount in the latter, allow the austenite existing at high
temperatures to be retained unchanged down to atmospheric
temperature.

The austenite so produced has properties which are in
many respects the same, no matter whether its retention
at room temperatures be due to the presence of chromium,
nickel or manganese or to combinations of them ; these
properties are moreover vastly different from those of
martensite. The latter constituent is intensely hard, having
a Brinell number of the order of 700, and more or less brittle.
It is magnetic and has a co-efficient of expansion not greatly
different from that of ordinary annealed steels in which the
dominating constituent is pearlite. Austenite, on the other
hand, is quite soft ; its Brinell number may be well below
200, but it often hardens very rapidly when cold-worked, so
much so that in some cases it is machinable only with the
greatest difficulty. The well-known " manganese steel,"
which contains twelve or fourteen per cent. of that metal

and is so frequently used for purposes such as tramway crossings on account of its great resistance to wear, is an example of an austenitic alloy which is commercially almost unmachinable. Austenite has a comparatively low yield point, often only about ten or twelve tons per square inch; it is also non-magnetic and frequently has a co-efficient of expansion about fifty per cent. greater than that of ordinary steel.

In order that austenite may be retained unchanged on cooling these high carbon chromium steels, both the chromium and carbon must be in solution in the iron and this only occurs when the steel containing them is heated to high temperatures; hence when such steels are quenched from a series of gradually increasing temperatures above Ac.1, they at first gradually get harder, reaching Brinell hardness numbers of 600 and upwards when quenched from about 1,000° C. The structure of
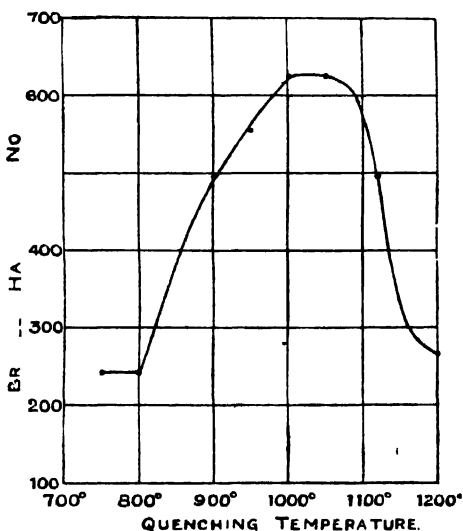
Fig. 32.   Brinell hardness numbers obtained on quenching steel containing 0·96 per cent. carbon and 13·1 per cent. chromium from the temperatures indicated.

such quenched samples consists of martensite together with large amounts of free carbide. When, however, the quenching temperature reaches a figure which is generally

between 1,100° and 1,200° C., the Brinell hardness number of the quenched sample suddenly falls to quite a low figure. The sample also acquires a characteristic microstructure and, in addition, is found to be non-magnetic. The hardness numbers obtained by quenching such a steel, containing 0·96 per cent. carbon and 13·1 per cent. chromium, from a series of temperatures are plotted in Fig. 82 and enable one to visualise ·the striking changes in the hardness value which are produced as the quenching temperature of such a steel is raised.

The carbon content required to retain austenite in a quenched sample varies with the amount of chromium present in the steel; with about 12 or 13 per cent. of the latter, however, the martensite in a specimen quenched from 1,200°C. will be partially replaced by austenite when the carbon reaches about 0·5 per cent. and the steel will be completely austenitic, after a like treatment, with 0·7 per cent. carbon or more.
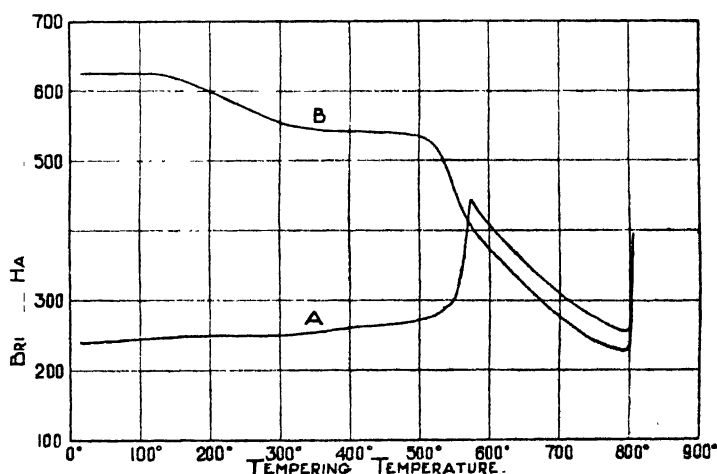
FIG. 33. Brinell hardness numbers obtained after tempering steel containing 1·01 per cent. carbon and 11·8 per cent. chromium.

Curve A—Samples previously quenched from 1,200°C.
Curve B   „   „   „   „   1,000°C.

A further point of interest with such austenitic steels lies in their behaviour on tempering. No appreciable effect is produced until the tempering temperature reaches about 550° to 600° C. At this temperature, the change from

austenite to martensite, which was suppressed when the material was quenched from 1,200° C., now takes place and, consequently, the material hardens when so tempered. Thus curve A in Fig. 33 represents the Brinell hardness numbers of samples of such a steel after tempering at gradually increasing temperatures and makes evident the very material increase in hardness obtained after tempering at about 600° C. The structure of such " hardened " samples consists of martensite, though generally this is accompanied by more or less troostite because the martensite formed by the tempering operation is itself very easily changed, as will be apparent from the rapid fall in hardness which occurs when the tempering temperature is raised somewhat higher (see Fig. 33).

On the other hand, when these high carbon steels are quenched from lower temperatures, e.g., 1,000° C. or thereabouts, giving Brinell hardness numbers of 600 or so, they consist of martensite, together with free carbide, and, on tempering, behave in a similar manner to the lower carbon steels. This is illustrated by curve B in Fig. 33, which was obtained from the same steel as curve A, but the samples had been previously quenched from 1,000° C. instead of 1,200° C. A comparison of these two curves also illustrates another effect of varying quenching temperature on stainless steel. It will be noticed that the samples quenched from 1,200° C. are harder than those quenched from 1,000° C. when both are tempered at temperatures above 600° C. This manifestation of a type of " red-hardness " is frequently produced in all high chromium steels ; it will be referred to later in connection with the mechanical properties of the steel.

As typical photographs of such high carbon steels, Figs. 28, 29, and 30 are included   Fig. 28 represents the structure of a steel containing 1·01 per cent. carbon and 11·8 per cent. chromium, when hardened and fully tempered (Brinell hardness number 241), and illustrates the large amount of carbide in such a steel ; the same steel quenched at 1,000° C. had a Brinell hardness number of 627 and the structure shown in Fig. 29 ; even at this temperature there is much carbide remaining undissolved. The importance of the effect of this carbide on the resistance of such material ·to corrosion will be indicated later. Fig. 30, is typical of the appearance of the constituent austenite in these steels.

High Chromium Irons and Steels. The data given in the preceding pages refer to material containing about 12 per cent. chromium. It was logical to commence the metallographical study of stainless steels by considering material of this composition because the first stainless steels used were of this type. It was also convenient, because the structural characteristics of steels containing this amount of chromium are simpler than those of higher chromium steels.

As the chromium content is raised, and particularly when it exceeds about 14 per cent., the properties of the material change in certain directions, the most important of the changes having reference to hardening capacity. Thus a higher quenching temperature is necessary to harden
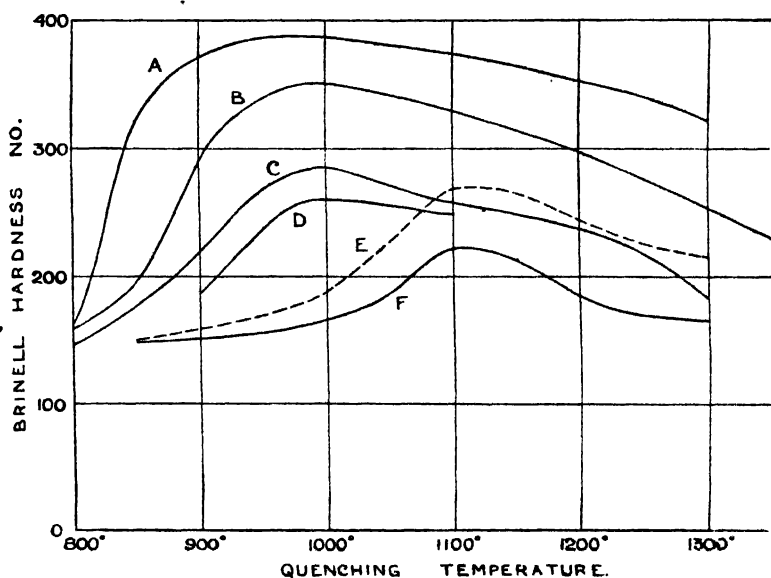
Fig. 34. Brinell hardness numbers of high chromium stainless irons after water quenching from the temperatures indicated.

Curve.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A.	0·09	0·23	0·18	12·3	0·32
B.	0·08	0·23	0·18	14·0	0·31
C.	0·10	0·36	0·22	15·5	0·39
D.	0·07	0·25	0·14	16·0	0·34
E.	0·13	0·31	0·20	17·2	0·14
F.	0·10	0·31	0·10	20·4	0·30
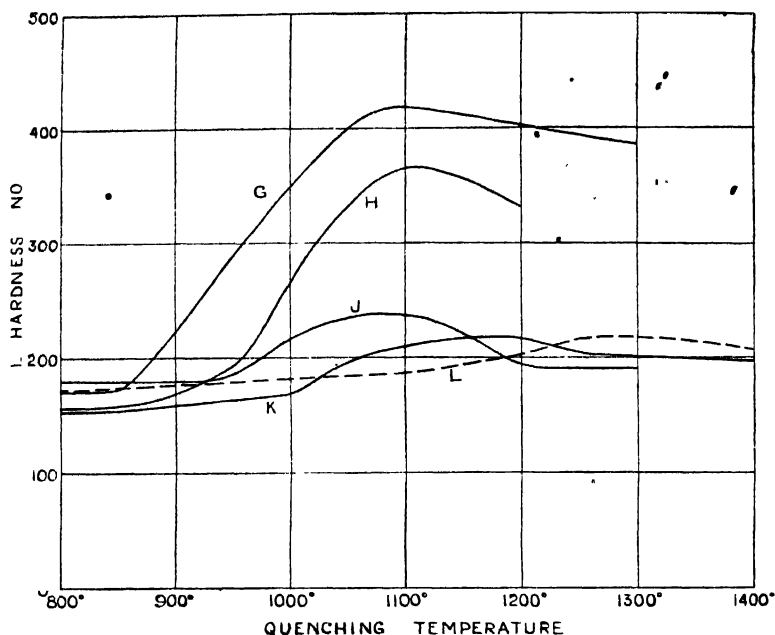
FIG. 35. Brinell hardness numbers of high chromium steels containing about 0·25% carbon after quenching from the temperatures indicated.

ırve.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
G.	0·17	0·26	0·18	15·9	0·31
H.	0·17	0·21	0·18	17·1	0·27
J.	0·23	0·36	0·18	19·9	0·27
K.	0·27	0·44	0·2	24·4	0·2
L.	0·37	0·54	0·2	29·5	0·2

the steel, as would be expected from the general effect of chromium in raising the temperature at which the Ac.1. change occurs and in retarding the solution of the carbide in the steel ; at the same time, the capacity of the material for hardening diminishes very markedly so that eventually, with a sufficiently high chromium content, the increase in hardness obtainable by quenching the steel in water from any available temperature becomes very small, even when as much as one per cent. carbon is also present. The effect of any given content of chromium varies with the amount of carbon in the steel, the lower carbon stainless irons losing their hardening power with a lower chromium content than the higher carbon steels. This is illustrated by the curves given in Figs. 34 to 37, which show the Brinell

hardness numbers of small samples of steels, containing various amounts of chromium and carbon, after they had been quenched in water from different temperatures. The curves in Fig. 34 relate to low carbon steels and indicate the marked falling off in the hardening capacity of such material when the chromium exceeds 14 per cent.
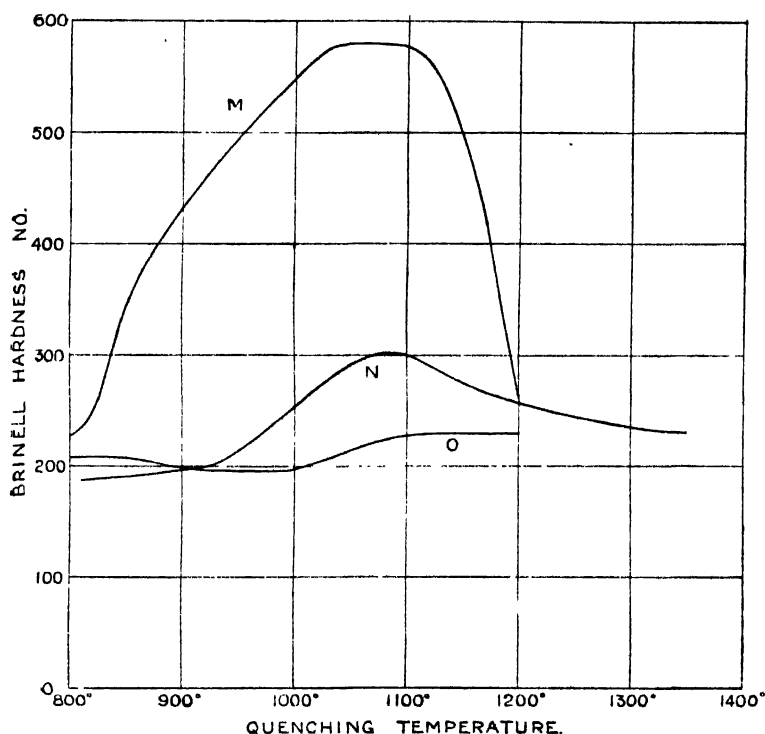
FIG. 36. Brinell hardness numbers of high chromium steels containing about 0·5% carbon after quenching from the temperatures indicated.

ırve.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
M.	0·53	0·22	0·29	16·8	—
N.	0·56	0·27	0·27	22·1	0·2
O.	0·42	0·78	0·32	25·0	0·48

In Fig. 35,* the results obtained from steels containing about 0·25 per cent. carbon are plotted ; those marked G and H may be compared with D and E in Fig. 34 when the

* Curves K, L, N, R, S and T in Figs. 35—37 are founded on data given by Kalling. (" The Austenatic Range in Chromium Steels." Jernkont Ann. 1927, p. 609.)

influence of the higher carbon content of the first two will
be obvious.   The remaining steels dealt with in Fig. 85,
those containing 20 per cent. or more chromium, harden
to a negligible amount only.   A rather higher carbon content
gives the results in Fig. 86.   Steel M hardens intensely when
quenched from 950°/1100°C. ; the rapid fall in the hardness
when still higher temperatures are used is due to the retention
of austenite in the quenched sample.   Raising the chromium
to 22·1 per cent. (curve N) reduces the maximum hardness
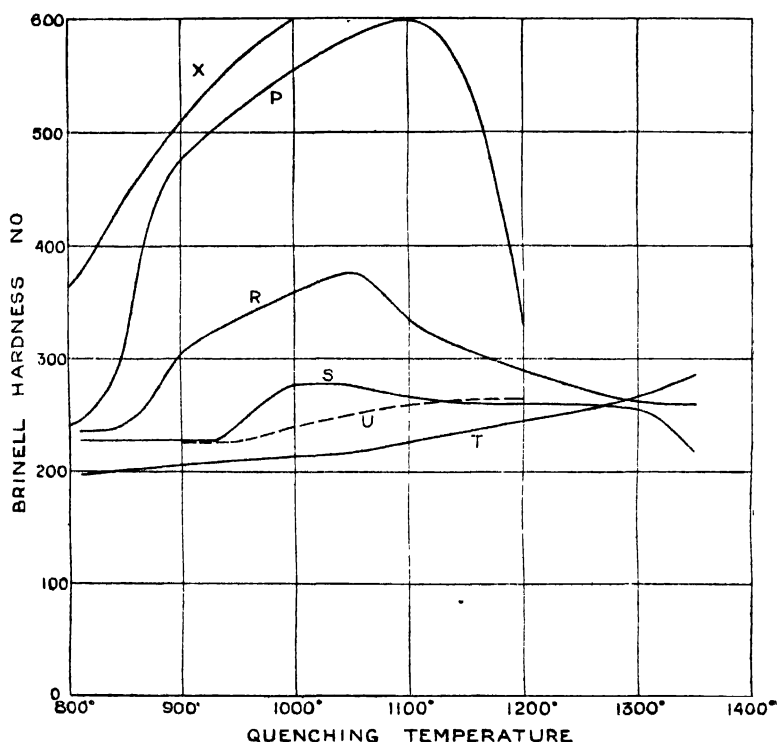
Fig. 37. Brinell hardness numbers of high chromium steels containing
more than 0·7% carbon after quenching from the temperatures indicated.

urve.	Carbon %	Silicon· %	Manganese %	Chromium %	Nickel %
P.	0·87	0·72	0·25	17·6	0·19
R.	0·80	0·65	0·54	22·0	0·00
S.	0·74	0·69	0·86	24·7	0·00
T.	0·77	0·32	0·2	26·3	0·20
U.	1·03	0·34	0·12	29·9	0·22
X.	1·9	0·91	0·27	27·5	0·36

attained to 300, while steel O, containing 25 per cent. chromium, only, reaches a figure of 228.

Fig. 27 shows that a similar state of affairs exists in steels of still higher carbon content.   Steel P (0·87 per cent. carbon, 17·6 per cent. chromium) behaves similarly to steel M; R (0·8 per cent. carbon, 22·4 per cent. chromium) reaches a hardness of about 375.   Increasing the chromium to 24·7 per cent. lowers the maximum hardness attained to about 280 (curve S); the two higher chromium steels T and U reach about the same hardness value but at considerably higher temperatures.   Curve X, however, indicates that intense hardening is produced at about 1000°C. in such very high chromium material if considerably more carbon is present.

A striking feature of the curves for the low carbon irons, plotted in Fig. 34, is that in all cases the Brinell hardness numbers rise to a maximum and then fall again as higher and higher quenching temperatures are used.   This fall in hardness is not due to the retention of austenite in the quenched sample, the cause of the similar but more pronounced effect produced in some of the high carbon steels (see Figs. 36 and 37) but to the progressive separation of ferrite.   The structural changes produced in the sample whose hardness values are plotted in curve A, Fig. 34, on quenching from temperatures up to 950°C. have already been described. Quenched from 825°C., the sample consisted of martensite and ferrite (see Fig. 25) and the amount of ferrite gradually decreased as the quenching temperature rose, see Fig. 26. The piece quenched from 950°C. consisted wholly of martensite, as did all the succeeding pieces quenched up to and including 1,150°C.   After quenching from 1,200°C., ferrite was again present and its amount increased as the temperature rose to 1,250°C. and to 1,300°C.

The 14 per cent. chromium iron, curve B, exhibited a similar solution and reprecipitation of ferrite but with a notable difference; in no case was a structure perfectly free from ferrite produced.   The minimum amount of this constituent was obtained in the samples quenched from 1,000°C. and 1,050°C., and in these it formed only a very small proportion of the whole.   There was noticeably more in that quenched from 1,100°C. and the amount increased progressively with still higher quenching temperatures.   The sequence of structural changes occurring in this iron are

illustrated in Figs. 38 to 43. These also show a further peculiarity of high chromium irons. As the quenching temperature rises to 1,250°/1,300°C., the grain size of the quenched sample gradually increases, as might have been predicted (one should note in this connection the higher magnification of Figs. 38 and 39 as compared with the others), but at 1,340°C. the structure becomes excessively coarse and also different in character from that previously found. In all the samples quenched below this temperature, the banded arrangement of the original bar was quite evident— the samples were polished and examined on a plane parallel to the length of the bar—but in that quenched at 1,340°C., this banding was entirely obliterated and replaced by an excessively coarse cellular structure.

The production of this coarse structure may be very conveniently observed by taper heating a short bar of stainless iron so that one end is raised to the melting point of the iron while the other end remains below about 700°C., and then quenching it in water. A bar ½ inch or ⅝ inch square is a convenient size and, after quenching, one face is machined or well ground to remove oxidation effects and then polished and etched. Fig. 44 represents, at twenty diameters, the structure of such a bar at a point about ¾ inch from the melted end ; it shows that the production of the coarse structure occurs quite suddenly, as though some internal change, such as occurs at Ac.1, had taken place in the material.

If the cooler end of the bar did not reach a higher temperature than 700°/750°C. before quenching, one can also trace along its length the whole sequence of changes occurring in the iron as the latter is heated to, and quenched from, higher and higher temperatures. Thus in the bar from which Fig. 44 was taken and which contained 15·5 per cent. chromium, one could see the production of martensite at the Ac.1. change and the gradual solution of the ferrite as the temperature rose above this, giving eventually a structure similar to Fig. 45. Still nearer the hotter end of the bar, the progressive coarsening of the grain size could be observed and also a gradual increase in the amount of ferrite ; then came the abrupt change in structure shown in Fig. 44 and, finally, the continuance of this coarse angular pattern up to the melted end of the bar.

Plate VII
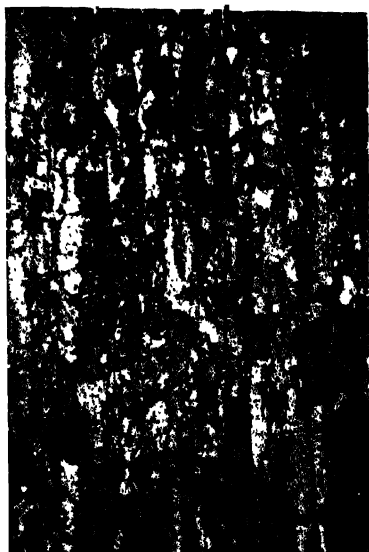
FIG. 38. Stainless iron, 0·08% carbon, 14·0% chromium. Water quenched 850°C. Brinell 196. × 300.
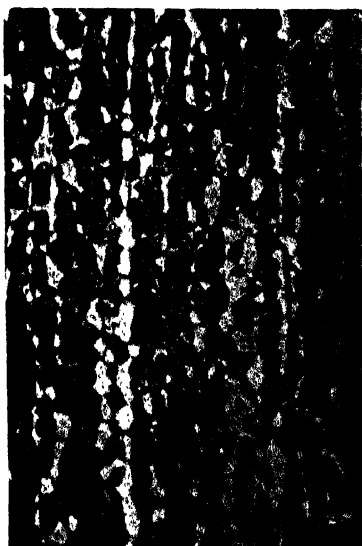
FIG. 39. Stainless iron, 0·08% carbon, 14·0% chromium. Water quenched 950°C. Brinell 340 × 300.

FIG. 40. Stainless iron, 0·08% carbon, 14·0% chromium. Water quenched 1050°C. Brinell 340. × 100.

FIG. 41. Stainless iron, 0·08% carbon, 14·0% chromium. Water quenched 1150°C. Brinell 321. × 100.

Plate VIII

Fig. 42. Stainless iron, 0 08% carbon, 14 0% chromium Water quenched 1250 C. Brinell 281   100

Fig 43 Stainless iron, 0·08% carbon, 14 0% chromium Water quenched 1340°C. Brinell 235   100
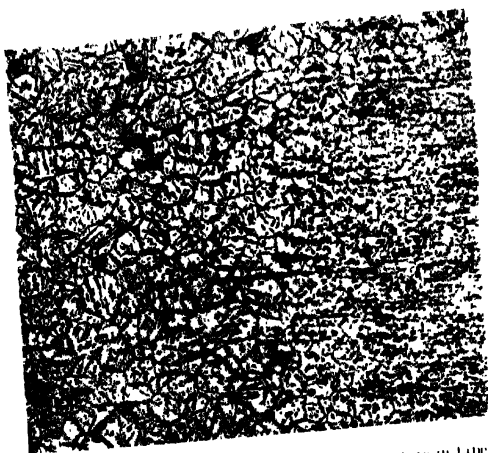
Fig. 44. Junction of coarse and fine structure in taper heated bar of stainless iron, 0 1% carbon, 15·1% chromium.

15.

Plate IX
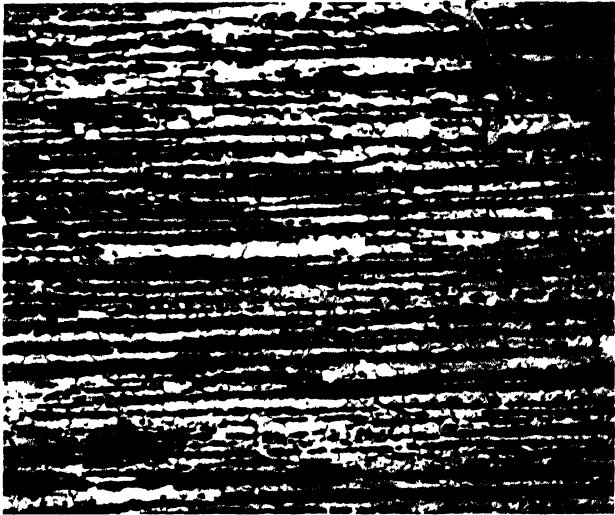
Fig 45   Stainless iron, 0·10% carbon, 15 5% chromium.   W.H.
1000°C. × 100.

Fig. 46.   Stainless iron, 0·13% carbon, 17·2% chromium.
W.H. 1100°C. × 100.

It may be noted that a coarse structure like that in Fig. 44 was produced near the melted end of a bar of stainless iron containing 0·08 per cent. carbon and 12·5 per cent. chromium, when treated in this manner; but neither the coarse structure nor the reprecipitation of ferrite at high temperatures was observed in a similar test on material containing 0·09 per cent. carbon and 9·9 per cent. chromium.

A sequence of structural changes similar to those described for the 14 per cent. chromium material, was obtained from irons containing still more chromium, except that these always contained considerable amounts of ferrite, no matter from what temperature they were quenched. Also the amount of martensite produced after similar treatment was less, the higher the chromium content.   For example, Figs. 45 and 46 refer to irons containing 15·5 per cent. and 17·2 per cent. chromium respectively, quenched in each case from the temperature giving maximum martensite content; they may be compared with Fig. 40.   The iron containing 20·8 per cent. chromium (curve F in Fig. 34) was still more preponderatingly ferritic.   The same effect may also be seen in Figs. 59, 62 and 63 (pages 85 to 87) representing the structures of various stainless irons as cast. Here the amount of ferrite is considerably greater, for similar chromium contents, than in the photographs just described, and for reasons which will be evident from the structural changes considered in the last few paragraphs, but again the amount increases as the chromium content rises.

It may also be noted from the curves in Fig. 34 that the temperature at which hardening commences rises with increase in chromium content, particularly when the latter is over sixteen per cent.   Also, up to this value, maximum hardness is obtained on quenching from temperatures in the neighbourhood of 1,000°C.   With 17·2 per cent. chromium, the corresponding temperature is 1,100°C.   The curve for the 20·8 per cent. chromium iron also shows a maximum at this temperature, but matters are complicated here by the fact that on quenching this material rapidly from still higher temperatures, austenite is preserved unchanged.   In the irons containing up to 17·2 per cent. chromium, maximum hardness corresponds in each case to a minimum amount of ferrite (and maximum of martensite) in the quenched sample. In the 20·8 per cent. material, the sample quenched from

1,200°C. contained least ferrite but it was accompanied by austenite instead of martensite and hence the hardness value of this sample is lower than that of the one quenched at 1,100°C.

A detailed description of these peculiar structural changes and of their cause would be out of place in this book, as it would involve a complicated study of the ternary iron-chromium-carbon equilibrium diagram—a diagram not by any means completely understood as yet—but it may be briefly stated that they are due to the fact that pure iron, in addition to the structural changes indicated in Fig.' 7, possesses a further one, occurring at about 1,400°C., at which the γ-iron changes to a form, called δ-iron, which is structurally the same as a-iron and probably possesses other similar characteristics, among them the power of dissolving only a very limited amount of carbon.

Chromium, when added to iron, lowers rapidly the temperature at which the change from γ-iron to δ-iron occurs. The effect on the temperature of the a to γ transition is not so marked ; probably additions of chromium up to 8 per cent. or so lower this temperature to some extent but, with still more chromium, it rises at an increasing rate, with the result that a perfectly carbonless iron-chromium alloy containing about 13 per cent. of the latter metal, would have no structural change at all. The temperature of the γ—δ transition would have fallen to such an extent that it would have reached the same value as that at which a-iron changes to γ-iron ; hence the latter would cease to exist and, as a-iron and δ-iron are structurally identical, no internal change would occur during heating or cooling. The exact chromium content needed to produce this effect has not yet been determined ; Maurer,* who investigated a series of iron-chromium alloys containing not more than 0·03 per cent. carbon, placed the disappearance of γ-iron at about 16 per cent. chromium. E. C. Bain,† however, considers that less chromium is required to effect this and places the limit at about 13 per cent. More recently, Oberhoffer and Kreutzer‡ have shown, by X-ray examination of the crystal structure, that γ-iron is produced up to about 15 per cent.

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* "Ueber den inneren Aufbau der Chromstahle." *Stahl und Eisen*, 1928, p. 999.

† "X-rays and Constituents of Stainless Steel." *Trans. A.S.S.T.*, Vol. XIV (1928), p. 27.

‡ *Stahl und Eisen*, Vol. XLIX (1929), pp. 189-190.

chromium but not beyond that amount. Kinzel* studied
the expansion of fine wires, of practically carbon-free material,
in a special form of dilatometer and found no evidence of
phase change when the chromium reached 12·5 per cent.
Kalling,† as a result of microscopic examination of quenched
samples of low carbon alloys, suggests as low a figure as
10 per.cent. for the disappearance of austenite from carbonless
alloys.   There is not as good agreement as might be wished
between the values obtained by the various investigators,
but in the present state of knowledge, a mean value of about
13 per cent. (or possibly somewhat lower) would appear to be
reasonably correct and this value has been adopted in Fig. 47,
which represents diagramatically the effect of chromium on
the A3 and A4 change points of iron.
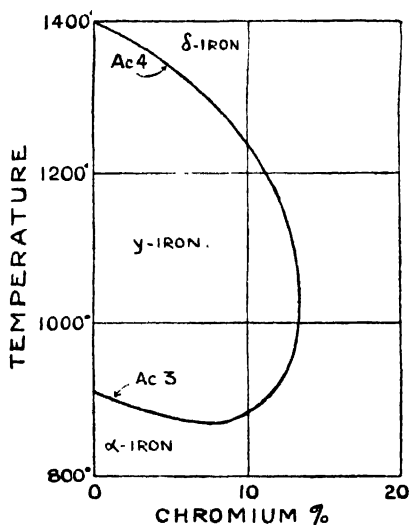
FIG. 47.   Effect of Chromium on the range of existence of γ-iron.

The range of existence of gamma iron, though it may
appear perhaps to be a rather abstruse question, is actually
of the greatest moment in the engineering application of steel.
The hardening of steel by quenching is made possible entirely
by the fact that carbon dissolves readily in the gamma form
of iron but is practically insoluble in any other form.   If,

owing to the addition of any other metal, the gamma form of iron ceases to exist in a particular steel, no appreciable solution of carbon can take place and hence no hardening of the steel by quenching is possible.   It may not be out of place, therefore, to note here that chromium is not alone among metals in thus restricting the range; of existence of gamma iron ; silicon, aluminium, tungsten and molybdenum behave in a precisely similar way, their action being indeed more effective than that of chromium.   Thus γ-iron ceases to exist in carbonless alloys of iron containing more than about 2·2 per cent. silicon, or 4 per cent. molybdenum or 8 per cent. tungsten.   Nickel, on the other hand, greatly increases the stability of γ-iron ; it lowers the temperature at which a-iron changes to the gamma form to such an extent that the latter becomes the stable form at atmospheric temperatures when the nickel content exceeds about 30 per cent.   Manganese and cobalt act in an intermediate way ; they do not diminish the range of existence of γ-iron nor do they noticeably increase it.   Interesting conclusions may be drawn from these facts ; it may be expected that the addition of nickel will notably improve the hardening of high chromium irons but that silicon, aluminium, tungsten, and molybdenum will have no such action ; on the contrary, these metals will most likely emphasise the effects of high chromium content which have just been noted.   The intermediate group, manganese and cobalt, are not likely to have much effect, one way or the other.   It will be shewn in a later chapter that these expectations are realised in practice.

Returning now to the iron-chromium alloys, if these contain carbon as well, even in small amounts, the action of chromium in preventing the formation of γ-iron is delayed. Hence in such alloys, containing over 13 per cent. chromium, a certain amount of austenite is formed, depending on the carbon content, and the alloy hardens to an extent which, with any given carbon content, diminishes as the amount of chromium in the alloy rises.

Similarly the hardening capacity of alloys containing equal amounts of chromium, above 13 per cent., increases with their carbon content. This may be observed by noting the curves in Figs. 84 to 37 relating to irons and steels of various compositions and comparing those of like carbon or chromium content.

The structural changes occurring in these high chromium steels and irons may be indicated in a qualitative, rather than a quantitative manner by Figs. 48 and 49.   The former shows at what temperatures this special form, δ-iron, is produced in ordinary steel.   In the lower part of this diagram, the structural changes previously described are plotted. Above the lines ABE, the steels consist of austenite, the solution of carbon in γ-iron.   The line EF represents the
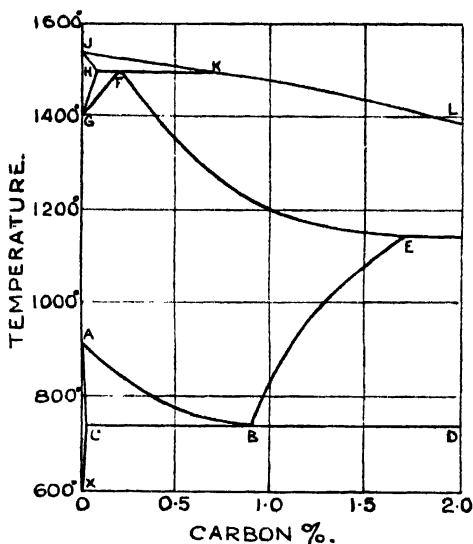
FIG. 48.   Iron-carbon diagram.

beginning of melting while G marks the temperature at which pure γ-iron changes to δ-iron.   The temperature at which this change occurs is raised very rapidly by even small amounts of carbon ; this is indicated by the very steep slope of the line GF.   Above this line, in the area FGH, the steel consists of a mixture of γ- and δ-iron, just as in area ABC there is a mixture of a- and γ-iron.   To the left of GH—in the area GHJ—all the iron exists in the δ condition, and the diagram shows that such iron can only dissolve rather less than 0·1 per cent. carbon.   Finally the line JHFE marks the beginning of melting, which is complete by the time the steel reaches the temperature corresponding to line JKL.   The line ACX indicates that ferrite dissolves a small quantity of carbon, probably not more than 0·08 per cent. at 700°C., and the amount decreases at lower temperatures.

It will be obvious that δ-iron is of very little importance in ordinary carbon steels; it is not formed if the carbon content of the steel exceeds about 0·2 per cent. and, in steels with less than this amount, only at temperatures between about 1,400° and 1,500°C. The effect of chromium on these somewhat complex changes is not known in sufficient detail to enable one to draw with certainty corresponding diagrams for iron-chromium alloys containing, for example, 10, 15 or 20 per cent. chromium, but broadly speaking, the changes in steel containing about 13 per cent. chromium and up to 1·0 per cent. carbon follow the lines in Fig. 49, these being lettered to correspond with those in Fig. 48.
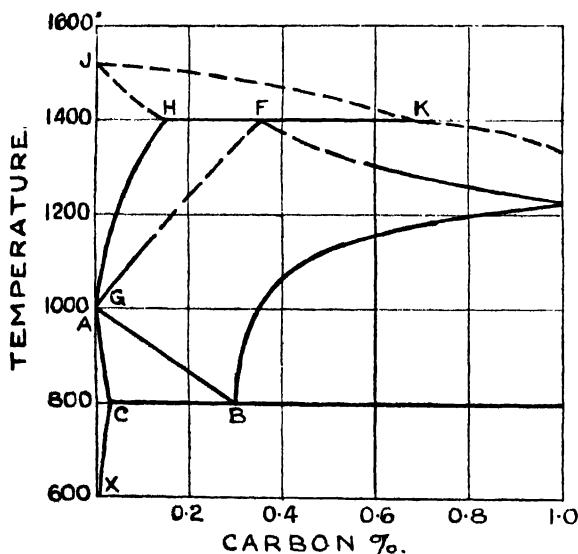
FIG. 49.   Effect of 13 per cent. chromium on the iron-carbon diagram.

·   This diagram of course summarises much of what has been discussed earlier in this chapter; for example, the raising of the temperature at which the Ac.1. change occurs and the reduction of the carbon content of pearlite—the eutectoid point B—from 0·9 per cent. to about 0·8 per cent. But it also shows that the range of existence of δ-iron is enormously increased as a result of the addition of chromium. Following what has been said in the last few paragraphs, the diagram indicates that a carbonless alloy containing 13 per cent. chromium possesses no γ-iron range at all, but that

the addition of carbon results in the formation of austenite. With only 0·1 per cent. carbon, or thereabouts, the range of temperature in which austenite exists alone is not very wide and as soon as the line GF is reached at about 1,100°C., δ-iron begins to separate out. The amount of the latter increases steadily until at 1,300°/1,350°C., line GH, austenite disappears, the whole mass becoming a solution of carbon in δ-iron. As regards lower temperatures, the position of ACX indicates that the solubility of carbon in ferrite at 800°C. or lower is not appreciably increased by the presence of 13 per cent. chromium.

The reader, on comparing this summary of structural changes with the series of photographs in Figs. 38 to 43 will notice some discrepancy between the description and the photographed structures. Thus the sample quenched at 1340°C. contains a marked amount of martensite instead of consisting solely of a solution of carbon in δ-iron ; on the other hand, there is a distinct amount of ferrite visible in the sample quenched at 1,050°C. in addition to the martensite of which it should consist entirely, if Fig. 49 be correct. With regard to the samples quenched from high temperatures and having the coarse cellular structures pictured in Figs. 43 and 44, it is very probable, practically certain in fact, that the martensite visible in these structures has been formed from austenite which has separated out during quenching, despite the rapidity of the latter. It will be noted that the martensite exists as a network round the grains of the ferrite and as barbs crossing the latter. This mode of occurrence is typical of material which has separated out of a solution during rapid cooling ; for example, when ordinary mild steel is cooled from above Ac.3. at a rate not quite fast enough to retain the whole of the ferrite in solution, a certain amount of this constituent separates out in a similar fashion to the martensite in Fig. 43. It would be very difficult to account for the difference in structural pattern between Figs. 42 and 43 unless it is assumed that the martensite in the latter had been formed from austenite which had ceased to exist at the higher temperature (1,340°C.) but had formed again on cooling therefrom.

The impossibility of obtaining a sufficiently rapid rate of cooling by water quenching small pieces is also largely the cause of the presence of some free ferrite in Fig. 40. A

contributory cause in this case may very probably be found in the difficulty of obtaining a perfectly homogeneous austenite in these steels at temperatures of 1,050°C. or so. No doubt at these temperatures the whole mass consists of austenite, i.e., a solution of carbon in γ-iron, but, owing to the slow rate at which the carbon diffuses in the steel, this austenite consists of bands alternately higher and lower in carbon than the average and it is at the points of lowest carbon concentration that the ferrite grains form, despite the rapidity of the quenching. Further reference to this banded structure will be found later (see pages 86, *et seq.*).

The line GF in Fig. 49 has been drawn as a dotted line over a large part of its course because sufficient data is not available to determine its exact position, particularly with regard to the maximum carbon content at which δ-iron is produced. The author has however noted the occurrence of a small amount of free ferrite in a steel containing 14·8 per cent. chromium and 0·24 per cent. carbon when quenched from a temperature just short of melting ; some δ-iron must therefore have been present at this temperature.

The position of the line GH in Fig. 49, as compared with the corresponding line for the iron-carbon diagram, means that the solubility of carbon in δ-iron (or, what amounts to the same thing, in a-iron) is increased considerably at temperatures above about 1,000°C. by the presence of chromium. Presumably the addition of more than 14 per cent. of this metal, e.g., 20 per cent., would lower still further the position of GH. The extra chromium would also very probably tend to raise the temperature at which Ac.1. and Ac.3. occur so that a simplified diagram for 18/20 per cent. chromium steels may be drawn roughly as in Fig. 50. This diagram indicates that austenite will not form at all unless the steel contains a certain minimum amount of carbon ; if less were present, it would dissolve directly in the alpha (or delta) iron, though prolonged heating at the necessary temperatures would most likely be necessary to secure equilibrium and even diffusion of the carbon. It seems probable, however, that this minimum carbon content is very low because appreciable amounts of austenite were formed in an alloy containing 20·4 per cent. chr mium and 0·10 per cent. carbon when quenched from temperatures in the neighbourhood of 1,200°C.; if, therefore, the solubility of carbon in the a-iron of this

alloy is less than 0·10 per cent at 1,200°C., it must be considerably smaller at 800°/900°C.

Line CBD in Fig. 50, as in Figs. 48 and 49, represents the beginning of the Ac.1 change, but in the former diagram the
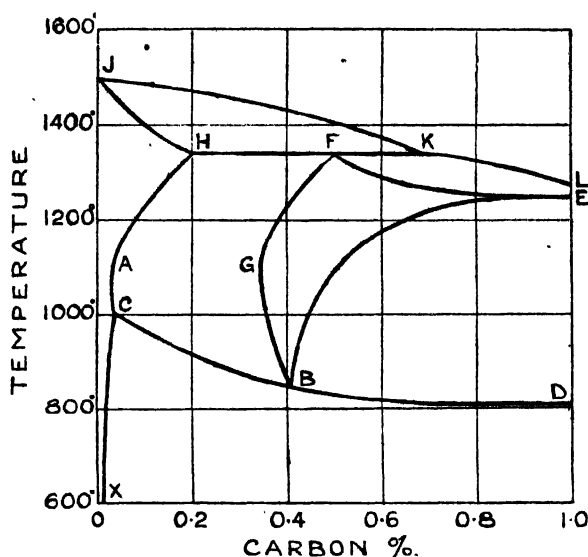
FIG. 50. Effect of 20 per cent. chromium on the iron-carbon diagram.

temperature is not independent of carbon content (as in Figs. 48 and 49) but falls as the latter increases. The reason for this is connected with the composition of the carbide in high chromium steels. It is known that this carbide consists largely of chromium carbide ; recent determinations, by B. Kalling,* of its composition indicate that it contains 5·3/5·4 per cent. carbon and about 68 per cent. chromium. It follows, therefore, that the higher the carbon content of a steel containing a given amount of chromium, the greater the amount of the latter locked up in the carbide and, hence, the smaller the amount dissolved in the ferrite of the steel when the latter is in the annealed or fully tempered condition.

As a result of the examination of a large number of steels containing up to about 30 per cent. chromium, Kalling concluded that the temperature at which Ac.1. occurs in steels containing more than about 15 or 16 per cent. of that

* Loc. cit.

metal, depends solely on the chromium content of the ferrite in the annealed or fully tempered sample. Thus he found that the Ac.1. change occurred at the same temperature in two steels containing (a) 0·18 per cent. carbon, 19·8 per cent. chromium and (b) 0·74 per cent. carbon, 24·7 per cent. chromium, due to the fact that the ferrite of both steels contained about 18 per cent. chromium, despite their wide difference in composition. Kalling's results indicate that the temperature of Ac.1. rises very rapidly, with increasing chromium content of the ferrite, when the latter exceeds about 15 per cent., his figures being approximately:

Calculated chromium content of ferrite	Temperature of Ac. 1.
14	810°C.
16	835°C.
18	900°C.
20	1000°C.
22	1170°C.

One may also note the effect of carbon content on material containing a given amount of chromium by comparing curves E and P in Figs. 34 and 37. These relate to steels containing 17·2 and 17·6 per cent. chromium, respectively, and the quenching tests on the higher carbon steel P show that the Ac.1 change in this material lies between 800° and 850° C. On the other hand, it is obvious from curve E (Fig. 34) that the lower carbon material is not hardened to any extent until the quenching temperature reaches about 1,000° C., although some evidence of change in this direction may be seen at 900° and 950° C. If Kalling's figures be accepted, the chromium content of the ferrite of these two steels is about 16 per cent. (E) and 7·5 per cent. (P) respectively.

Above the temperature, marked by CBD, and with less carbon than is indicated by BGF, the steels consist of mixtures of ferrite and austenite together with any undissolved carbide. The reversal of slope of the line at G indicates that the amount of austenite, in any particular steel, reaches a maximum at this temperature and thereafter decreases as the temperature rises still higher. To the right of BGF, the steels consist of austenite, together with free carbide at still higher carbon contents. Probably the most striking feature of Fig. 50 is the extensive range of carbon content and

temperature in which the structure is heterogeneous, consisting of mixtures of austenite and a (or δ) iron. Notice also that the temperature at which melting commences, HFE, has fallen with increase in chromium content.

It is admitted that Fig. 50 is largely speculative because the structural conditions existing in such high chromium alloys are still rather obscure. A factor which increases the difficulty of determining an equilibrium diagram for these steels is the very slow rate at which the particles of carbide, which they contain, react with the ferrite surrounding them and constituting the bulk of the material. Determinations of the temperatures at which structural changes commence in these high chromium steels, and made by examining samples quenched from a series of ascending temperatures, are therefore likely to be in error unless ample time is allowed at each temperature for the steel to attain something approaching equilibrium before it is quenched. For example, O. V. Greene* records that the first appearance of austenite in quenched samples of steel containing 0·33 per cent. carbon and 20·4 per cent. chromium was lowered 110°C. (from 1,040° to 930°C.) by increasing the time, during which the samples were maintained at their respective temperatures before quenching, from twenty to sixty minutes.

One may suggest a reason for this by again comparing the two steels, E and P, mentioned previously. The ferrite of the higher carbon steel, P, contains about 7·5 per cent. chromium ; it will therefore have a gamma range of its own and, hence, will not behave in a very different manner from the 12/14 per cent. chromium steels described in the earlier part of this chapter. On the other hand, the ferrite of the lower carbon iron, E, will contain about 16 per cent. chromium in solution ; it will therefore have no gamma range of its own and the formation of austenite in this iron, when it is heated above the theoretical temperature of the Ac.1 change, will be extremely sluggish. One may suppose that a slow action takes place at the interface between each carbide particle and the ferrite surrounding it ; a nucleus of austenite is slowly formed by the diffusion of the carbide and this nucleus gradually dissolves the ferrite in its immediate vicinity. One might almost regard the action as being due to the carbide dissolving the surrounding ferrite.

* *Trans. A.S.S.T.*, July, 1930, p. 45.

What is the practical importance of these complex changes ?   The engineer may perhaps concede that the elucidation of the effect of chromium on the range of existence of γ-iron forms an interesting theoretical study for the metallurgist, but he may reasonably enquire as to what practical value can be placed upon such speculations ; for it must be admitted that Figs. 49 and 50 are largely speculative, although they are reasonable explanations.   Actually the practical effects of these complex changes are very great. Reference has already been made to the fact that the hardening of steel by quenching is impossible in the absence of γ-iron ; but its absence also affects the general behaviour of the steel as may be shown by considering a stainless iron containing 0·1 per cent. carbon and 17 or 18 per cent. chromium.   A bar of this which has been rolled or forged and afterwards tempered at about 700° C., in the same way that one would temper a lower chromium stainless iron, will consist of grains of ferrite through which are dotted particles of carbide.   These grains of ferrite, owing to their high content of chromium, no longer possess a change point ; they do not give rise to γ-iron when heated and hence have not the property of being refineable by heat treatment.   In other words, they behave in the same way as copper instead of iron and if, by any chance, they become coarse grained, e.g., by heating to too high a temperature, they can only be refined again by mechanical work, such as rolling or forging. Owing to its lack of response to heat treatment processes, the hot working of such a steel assumes an added importance as it will largely control the structural characteristics and, hence, the mechanical properties of the finished material. As these conditions apply, in greater or less degree, to all materials whose composition is such that they do not become completely austenite in any temperature range (and Fig. 50 indicates that this range of composition is extensive), it is important that the dependence of properties on carbon and chromium content be determined.

It follows as a result of these structural changes in high chromium steels that the latter may be divided into three groups :—

(1) those which do not harden appreciably and are not refineable by heat treatment ;

(2)   those which harden well and may be refined by heat treatment in a similar manner to the stainless irons and steels of lower chromium content;

(3)   an intermediate group which hardens to a limited extent and is partially susceptible to heat treatment processes.

From the point of view of resistance to corrosion, group (1) is the most desirable because that part of the chromium which exists in the steel as chromium carbide does not exert any beneficial influence on the resistance of the metal to corrosion.   On this count, therefore, carbon should be kept as low as possible.   Unfortunately, however, the mechanical properties of most of these low carbon materials are deficient in certain important respects.   For example, with a carbon content of the order of 0·1 per cent., those which contain up to about 14 per cent. chromium belong to group (2); above about 16 per cent. to group (1).   Group (3) consists of alloys with compositions between these two values. Considering for the moment those containing over 16 per cent., their lack of hardening power is not, in itself, particularly serious ;   it may be an advantage for some engineering purposes.   The impossibility of refining by heat treatment operations is of much greater moment, because the fragility of these irons increases markedly when their grain size becomes coarse.   Not only does this imply that a close control must be kept on forging and rolling temperatures but also that the ductility of the material, when in the form of bars or forgings of large size, is likely to be considerably inferior to that of small-sized pieces, owing to the impossibility of producing as fine a grain size in the article of large sectional area.   The bad effects of coarse grain size are also evident, sometimes painfully so, when the material is welded. On each side of the weld there is produced a band possessing a structure similar to that in Fig. 43, and as it is impossible to refine this structure by any form of heat treatment, welding operations on these high chromium irons are seldom very satisfactory.

A further disadvantage of these materials, and one that may probably be traced back to their structure, is the very pronounced grain growth to which they are subject if held at a red heat for long periods.   One of the useful properties of high chromium irons is their resistance to oxidation when

heated to relatively high temperatures ; their usefulness as heat-resisting steels is, however, limited in certain directions by the excessively coarse structure which is produced during use and the brittleness which this entails.   It is very likely that the readiness with which very large grains form in these irons is not unconnected with their relative freedom, at high temperatures, from austenite.   The latter, if present in any quantity, would obstruct the growth of the ferrite grains. Pure iron, for example, when cold worked and then annealed at temperatures between about 700° and 900°C. frequently exhibits a very striking growth in the size of its ferrite grains ; if, however, a mild steel containing 0·15 or 0·20 per cent. carbon is treated in the same manner, the increase in grain size is much less marked.   The reason is not far to seek ; the ferrite grains in the pure iron are free to re-orient themselves and grow in size without hindrance from any other structural constituent, but those in the mild steel are obstructed by the grains of austenite which form on heating at about 740°C. and which gradually absorb the ferrite surrounding them as the temperature rises above this.   For the same reason, the grain growth which is so marked a feature of the high chromium irons, does not occur to anything like the same extent in those of lower chromium content.

From an engineering standpoint, however, the most serious defect of these high chromium irons is their notch brittleness.   This aspect of the matter will be treated in some detail in the next chapter, but it may be mentioned here that stainless irons containing up to about 14 per cent. chromium, when properly heat treated, possess very high Izod impact values ; on the other hand, those with 16 per cent. or over have values of the order of 5-ft. lbs. or less, nor can this value be improved by any form of heat treatment.   Between 14 per cent. and 16 per cent. chromium, the impact value may vary greatly in different casts of the material and is not predictable from their analyses.

As regards the higher carbon material, Fig. 51 gives, according to E. C. Bain,* the relation between carbon content and hardening capacity of high chromium steels.   Those containing less carbon than is indicated by curve AB do not harden ; those with more than corresponds to line CD

* "X-rays and the Constituents of Stainless Steels." *Trans. S.SA..T.*, July, 1928, Vol. XIV, p. 27.

harden fully. When the composition falls between the two curves, the steel hardens partially. Curve XY was obtained by Kalling* and gives the minimum amount of carbon
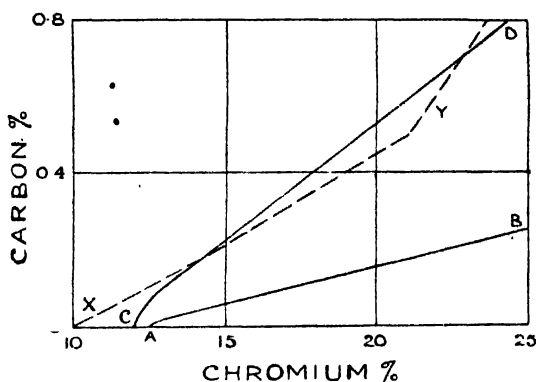
FIG. 51. Effect of carbon content on hardening capacity of high chromium steels; see page 78.

required, with the chromium contents indicated, to produce steel which shall contain no free ferrite after suitable quenching. This curve agrees very well with that (CD) given by Bain for steels which harden fully. It should be noted that the positions of the curves AB and CD are only approximate
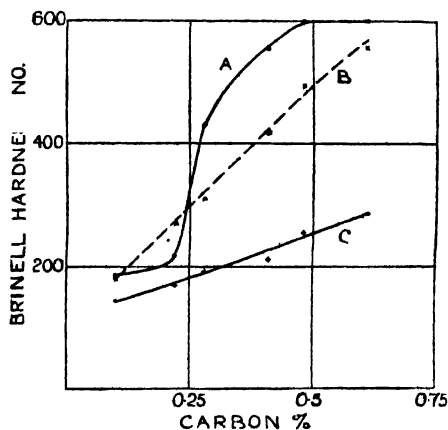
FIG. 52. Effect of carbon content on hardness values of 17 per cent. chromium steel.

Curve A—Bars 2 in. sq. cooled from a forging heat, about 1,100°C.
  ,,   B— ,,   1⅛ in. diameter O.H. 950°C.
  ,,   C— ,,   1⅛ ,,   ,,   ,,   ,,   T. 700°C.

* Loc. cit.

as there is no sharp line of division between the several groups. This is illustrated by the curves in Fig. 52, in which are plotted results obtained from a series of steels containing 17 per cent. chromium. Curve A relates to the Brinell hardness values given by bars two inches square after being cooled freely in the air from a forging heat, about 1,100°C. For curve B, bars 1½ inch diameter were quenched in oil from 950°C. ; curve C gives the further results from the same quenched bars after they had been tempered at 700°C. The impossibility of fixing a limiting carbon content which shall separate hardening and non-hardening steels will be obvious. At the same time, the author's experience suggests that the non-hardening range of composition extends to somewhat higher carbon contents than are shown by curve AB ; witness, for example, the results plotted in Fig. 36 relating to steel O, containing 0·42 per cent. carbon and 25 per cent. chromium. The curve would certainly need altering in this manner if it were to include all alloys which are not refineable by heat treatment.

The structural conditions existing in iron-chromium alloys containing more than about 25 per cent. of the latter metal are still rather obscure. Bain and Griffiths* have shown that low carbon alloys containing about equal amounts of iron and chromium normally consist of something in the nature of ferrite, together with free carbide. When, however, they are drastically annealed or are heated for long periods at temperatures between about 500° and 800°C., they transform into a hard and very brittle material which these investigators call the " brittle constituent."† This constituent may also be produced in alloys containing down to about 30 per cent. chromium under similar conditions. Bain and Griffiths quote an example of such a chromium iron which was made brittle by several months' exposure at about 550°C. Microscopical examination suggested that, in this case, the brittle constituent formed a network round the grains of ferrite ; it was removed by reheating to about 900°C. and cooling rapidly, with consequent improvement in the mechanical properties of the material. Descriptions of

* " An Introduction to the Iron-Chromium-Nickel Alloys." *Trans. Amer. Inst. Min. & Met. Eng.*, 1927, Vol. 75, p. 166.

† Recently Bain and Aborn (" The Nature of the Nickel-Chromium Stainless Steels." A.S.S.T., Sept. 1930) have suggested that the formation of this brittle constituent may be due to nitrogen.

the structure and properties of some of these very high chromium steels, after various forms of heat treatment, will be found in papers by C. E. MacQuigg,* Kalling,† and Krivobok and Grossmann,‡ to which, as well as to the paper by Bain and Griffiths mentioned above, those interested may be referred.

A further interesting effect of the comparatively wide range of existence of δ-iron in stainless irons and one, moreover, of considerable practical importance, relates to the production of decarburised skins on such material. As has been already mentioned, high chromium steel possesses a notable resistance to scaling and oxidation when exposed to high temperatures ; for example, the ordinary stainless steel used for cutlery purposes and containing 12 or 14 per cent. chromium, does not scale appreciably when heated, even for prolonged periods, at any temperature up to about 800°C. Increasing the chromium content to 20 per cent. or thereabouts, raises the non-scaling range to about 950°C., while resistance to still higher temperatures may be obtained by further additions of the metal. At temperatures above these respective limits, however, the high chromium steels scale in much the same way as ordinary steels and, also like the latter, their surfaces when so heated become decarburised to a greater or less extent. The decarburised skin generally produced on the higher carbon steels and also, up to certain temperatures, on stainless irons is of a similar type to that found on ordinary carbon steels ; there is a gradual decrease in carbon content as one approaches the extreme surface from the body of the steel. If, however, stainless irons are reheated above a certain minimum temperature, which depends on the amount of chromium they contain, decarburisation leads to the production of a sharply defined low carbon band of coarse ferrite grains which grow from the surface and possess a columnar structure very similar to that associated with hot cast ingots. Figs. 53, 54 and 55 show the decarburised zones produced on samples of 14 per cent. chromium iron after reheating for twenty minutes to 1,050°, 1,150° and 1,250°C. respectively ; prior to this treat-

* "Some Commercial Alloys of Iron, Chromium and Carbon in the Higher Chromium Ranges." *Trans. Amer. Inst. Min. & Met., Eng.*, August, 1923.

† *Loc. cit.*

‡ "A Study of the Iron-Chromium-Carbon Constitutional Diagram." *Trans. A.S.S.T.*, July, 1930, p. 1.

ment, the samples had been machined all over to remove any pre-existing decarburisation. The difference between Figs. 53 and 54 is understandable if one assumes that the $\gamma - \delta$ change occurs in very low carbon iron, containing 14 per cent. chromium, at some temperature between 1,050° and 1,150°C. At the former temperature the decarburised skin still consists of γ-iron, similar to the remainder of the sample; hence there is nothing to prevent the free diffusion of carbon from more deep seated layers into the decarburised zone, and one would expect to obtain a continuous gradient in carbon content from the skin until the normal percentage in the sample was reached. At 1,150°C., on the other hand, the decarburised skin automatically becomes δ-iron and, as the carbon content of successive layers is reduced by the requisite amount, these also change to δ-iron. Each successive layer being thus formed upon a layer of existing crystals of δ-iron, assumes the orientation of the latter, causing these to grow in the same way that a crystal of alum, for example, grows when suspended in a saturated solution of that salt. Hence the layer of δ-iron crystals first formed grows into the body of the material, developing the characteristic columnar form visible in Figs. 54 and 55. Moreover, as the δ-iron has a different crystalline form from γ-iron and can only dissolve a very limited amount of carbon, the inner surface of the decarburised layer is very sharply defined, both in structure and carbon content, from the normal material inside. This is one of the most striking features of Figs. 54 and 55.

A similar decarburised layer was produced on iron containing 12·3 per cent. chromium at 1,200°C. but not at 1,150°C. With 15·5 per cent. chromium, the temperatures were 1,050° and 1,000°C. respectively.

It should also be noted that this sharply defined band is not evident if the iron has been heated to a sufficiently high temperature to form the coarse cellular structure shown in Figs. 43 and 44. At these high temperatures, the whole mass of the material probably consists of a solution of carbon in δ-iron. The decarburised band has therefore a similar structure to the bulk of the sample and, while evidences of the columnar type of structure are often still visible in it, there is no longer the sharp contrast both in structure and carbon content, between the band and the material adjoining it, that is·so noticeable in Figs. 54 and 55.

Plate X

FIG. 53. 14% chromium iron. Decarburised skin of sample heated to 1050 C. × 75.
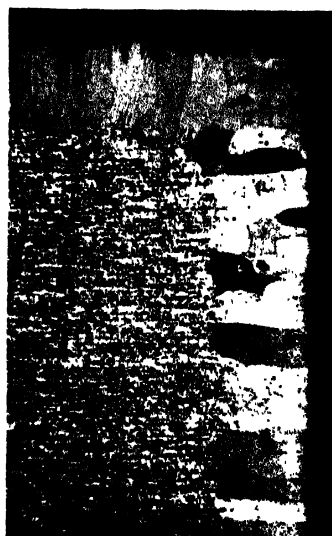
FIG 54 14% chromium iron Decarburised skin of sample heated to 1150°C × 25.

FIG. 55. 14% chromium iron. Decarburised skin of sample heated to 1250°C. × 25.

FIG 56. Steel containing 0 67% carbon; 14·1% chromium Decarburised skin on sample heated to 1300°C. × 100.

The very great depth of these decarburised skins should also be observed ; in the sample shown in **Fig. 55,** this amounted to nearly one sixteenth of an inch.   The production of these very deep decarburised layers, even in such a short time as twenty minutes and under conditions which were not particularly oxidising, is not only important from a practical standpoint, but also should be very carefully borne in mind by those carrying out investigations on the structure, at high temperatures, of steels containing large amounts of chromium.   It is probable that more than one investigator has been misled as to the structural changes taking place in these steels owing to the great depth of the decarburised skin not being realised ; as a consequence, sufficient material has not been removed, by grinding or machining, from the surfaces of heat-treated samples when these have been prepared for microscopical examination. Hence the structural conditions existing in the skin have been observed during this subsequent microscopical examination and have been unwittingly regarded as representing those existing in the undecarburised portion.

Obviously the production of a skin similar to those in Fig. 54 or 55 is possible on high chromium steel of any carbon content, providing the surface layer is decarburised to a sufficient extent to produce δ-iron.   Fig. 56 for example represents a section through the skin of a small piece of steel containing 0·67 per cent. carbon and 14·1 per cent. chromium after reheating to and quenching from 1,200°C.   The structure of the undecarburised portion of this sample consisted of practically pure austenite—see Fig. 30 (page 54). The first effect of decarburisation was the production of martensite grains among the austenite and the former gradually replaced the latter as the carbon contents decreased.   Then some ferrite appeared and finally the sharply defined band of practically carbonless δ-iron shown, together with the adjoining martensitic area, in **Fig. 56.**

Macrostructure and Ingot Heterogeneity.   In the preceding pages, the changes produced by different conditions of heat treatment on the structure of high chromium steel have been considered on the tacit assumption that such material was homogeneous in character, i.e., that the chromium, carbon and other elements present in the steel were evenly distributed through the iron, or, at least,

in a sufficiently even manner as to approximate to a homogeneous condition for practical purposes. It is important, however, to see whether such a condition actually exists and if not, to what extent the structure of the steel departs from homogeneity.

It is well known that when ordinary carbon steel solidifies from the fluid condition, the portions of each separate crystal which freeze out first contain a smaller percentage of dissolved impurities, such as carbon, silicon, manganese, phosphorus, than the fluid steel from which they separate, and that, as freezing gradually progresses, material containing a gradually increasing amount of such impurities is deposited, the portions which finally freeze being much more impure than the original fluid metal. During and after freezing, diffusion takes place rapidly with regard to the carbon, so that the original distribution of this element in the solid material is to a very great extent obliterated. The other elements present, however, diffuse much more slowly, if at all, and hence the original crystalline structure produced during the freezing process may be shown in ordinary steels by the use of special etching reagents which attack the steel in a manner depending on the concentration of these dissolved impurities. By the use of such reagents as, for example, the various " copper " reagents developed by Rosenhain, Stead, Le Chatelier and others, or the still more striking method of macro-etching described by Humphrey,* the purer dendrites which solidified first are attacked in preference to the more impure areas and, as a result, one obtains a dendritic structure similar to Fig. 57, which shows very clearly how the crystalline mass of the steel was built up. Etching the same section with the ordinary reagents used in the microscopic examination of steel, such as a 5 per cent. solution of picric acid in alcohol, reveals merely the distribution of carbon in the steel when cold; and, as the carbon during and immediately after solidification has diffused, producing an austenite practically homogeneous with respect to this element, which has afterwards split up at the critical changes into pearlite and ferrite or cementite, the patterns produced by the two types of reagents often bear little apparent relation to each other. During any subsequent heat treatment operations, the original distribution of the

* *J.I S.I.*, 1919, I, 273.

Plate XI

Fig. 57. Dendritic structure of ordinary carbon steel ingot.

Plate XII
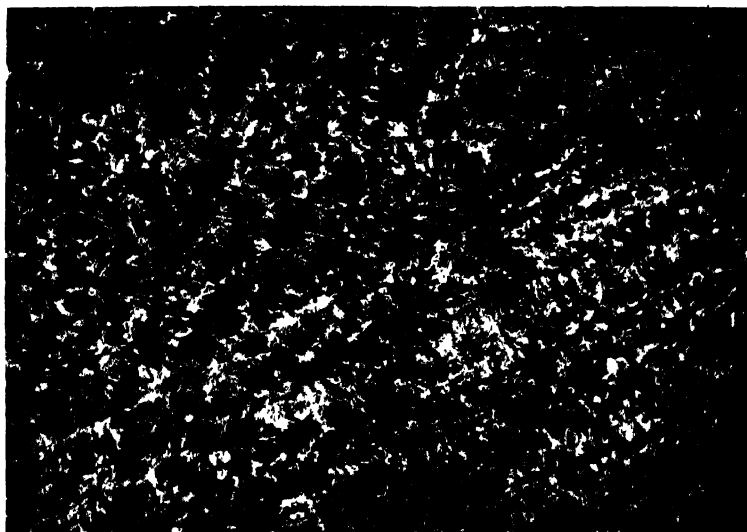
FIG. 58 Dendritic structure of cast sample of stainless steel (0.42 per cent. carbon, 12 per cent. chromium), slowly cooled after casting   50.

FIG. 59. Dendritic structure of ingot of stainless iron: 0.07 per cent. carbon, 11.7 per cent. chromium × 50.

impurities other than carbon is practically unaffected.   Even
rolling or forging operations do not remove this pattern
but merely distort it to a greater or less degree.   On the
other hand the carbon distribution, as shown by the ordinary
pearlite and ferrite or cementite structure, is modified every
time the material is heated and cooled through the change
points.   In any, piece of ordinary carbon steel, therefore,
there are two structures more or less independent of each
other ;   the one shows the state and distribution of the
carbon in the steel, and forms the ordinary micro-
structure ;   the other indicates the original crystallisation
of the ingot, produced on solidification and more or less
distorted by subsequent mechanical work, and is generally
referred to as the " macrostructure," its pattern being fairly
coarse and visible to the unaided eye.

The presence of the large amount of chromium in
ordinary stainless steel so retards the diffusion of the carbon
that the distribution of this element in a cast sample of the
steel, when cold, outlines the original dendritic structure
produced on solidification, and not only so, but this structure
persists to a marked extent even through the operations of
forging and rolling.   For example, in ingots or castings,
which have been cooled down after casting at a sufficiently
slow rate to soften the material completely, the original
dendritic structure is shown very markedly by the distribu-
tion of the carbide   Thus Fig. 58 shows the structure obtained
with such a sample containing 0·42 per cent. carbon and 11·3
per cent. chromium ;   it will be seen that the dendrites which
solidified first contain less carbide than the interdendritic
filling which froze later.   A similar sample cooled quickly
after casting consisted of a mixture of martensite and
austenite, the former occupying the position of the dendrites
while the latter occurred in the interdendritic filling, the
carbon concentration there being sufficiently high to cause
the complete suppression of the change points on rapid
cooling and the consequent retention of austenite.   Similar
dendritic structures may be obtained with the low carbon
stainless iron, thus Fig. 59 shows the structure of
an ingot containing 0·07 per cent. carbon and 11·7
per cent. chromium and consists of ferrite and martensite.
This dendritic structure is very persistent even after drastic
heat treatment.   As examples of this, Figs. 60 and 61 are of

interest; the former represents the structure of a sample similar to that represented in Fig. 58, after annealing for four hours at 1,100° C.; the latter shows that of a bar, 1½ inches diameter, of similar analysis to the cast sample described above, after the forging and rolling operations necessary to reduce it from an ingot 12 inches square. In both cases the dendritic structure is clearly evident. Both these examples are of steels in the annealed condition, and the structure obtained by such treatment emphasises the distribution of the carbide in a more marked manner than when the material is hardened or hardened and tempered; the rather high carbon which the samples contain also helps in retaining the original heterogeneity; however, they serve to emphasise the effect of the chromium in retarding the diffusion of the carbon in the steel.

It will be evident from the examples given above that there is likely to be evidence of a certain degree of heterogeneity in all samples of high chromium steel. During rolling or forging operations, the original dendritic structure with its variations in composition is distorted and drawn out to a greater or less extent into fibres or thin plates, depending on the section of the bar into which the material is being worked. Each reheating for mechanical work affords opportunity for diffusion to take place to some extent, while the actual forging and rolling, by reducing the cross sectional area of the original dendrites, reduces the distance through which diffusion has to take place and thereby helps it considerably. As far as the author is aware no estimation of the amount of heterogeneity, due to the original dendritic structure, existing in a rolled or forged product of stainless steel has been made; but although it can be detected in different ways, even in material which has been reduced in cross-section to a considerable extent, it is probable that its amount is considerably less than it was in the ingot form.

The presence of this heterogeneity may be shown very strikingly in the ordinary " cutlery " type of stainless steel, containing 12/14 per cent. chromium and 0·3 per cent. carbon, by quenching the steel from a temperature not quite high enough to dissolve the whole of the carbide; in which case in a longitudinal section, the carbide remaining out of solution will tend to be arranged in chains or streaks

Plate XIII

FIG. 60. Similar sample to that shown in Fig. 58 after annealing for fou hours at 1,100°C.; the dendri structure is still prominent. × 50.
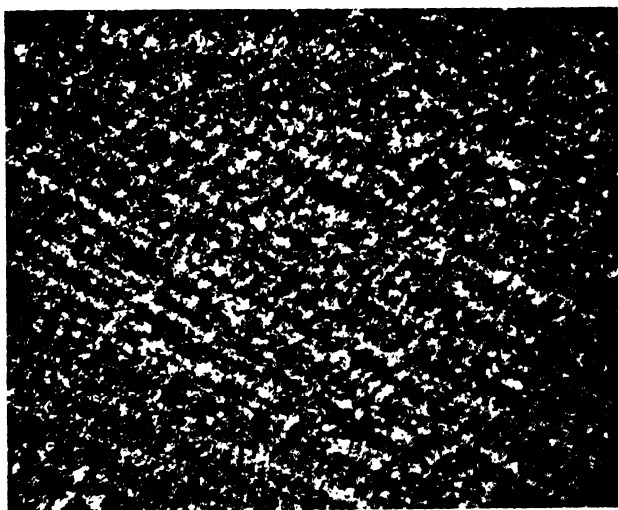
FIG. 61. Remnants of the original dendritic structure visible in a rolled bar, 1½-ins. diameter, of stainless steel. × 100.

Plate XIV

Fig. 62. Ingot structure of stainless iron, 0.07% carbon, 16.0% chromium. × 20

Fig. 63. Ingot structure of stainless iron, 0.10% carbon, 20.4% chromium × 20.

Fig. 64. Banded structure of Stainless iron plate, 15% chromium. × 60.

separated by other streaks which are practically free from carbide   It may also be disclosed by slowly cooling the steel from a similar temperature ; in this case the streaks in which the carbide had been taken completely into solution will have a pearlite structure while the alternating streaks, where some carbide remained undissolved at the annealing temperature, will contain globular carbide.

When considering what effects these remnants of the original ingot structure have on the properties of the rolled or forged product, it is convenient to divide the high chromium materials into two groups ; those which are refineable by heat treatment methods and those which, owing to their high chromium and low carbon contents, are not completely refineable.   The latter always contain large amounts of free ferrite, no matter how treated.

In the case of the first group, it is somewhat doubtful what effect these remnants of ingot heterogeneity have.   Like all other steels, those of this group exhibit evidences of " fibre " in rolled or forged products, but it is probable that this is due in much greater degree to slag and other non-metallic inclusions in the steel than to these drawn-out remnants of ingot crystals.   It may be accepted that, when properly made, chromium steels of this type behave in this respect in much the same manner as ordinary structural alloy steels ; they exhibit a similar degree of " fibre."

In the case of the higher chromium alloys, which cannot be completely refined by heat treatment, matters are rather different.   An ingot of stainless iron, for example, containing 15 or 16 per cent. chromium has a structure similar to Fig. 62, i.e., very large grains of ferrite with a small amount of martensite or sorbite, depending on its rate of cooling.   A still higher chromium content, e.g., 20 per cent. produces a cast structure still more preponderatingly ferritic, as shown in Fig. 63.   When ingots of materials such as these are reheated for forging or rolling operations, the carbon has even less opportunity for becoming evenly distributed throughout the steel than it has with lower chromium material, because at no temperature is there obtained a structure consisting entirely of austenite ; some ferrite always remains undissolved.   Hence there is produced, in rolled or forged products, a sandwich-like structure consisting of bands of

ferrite, practically free from carbon, alternating with other bands containing variable amounts of carbide, either in or out of solution. A typical appearance found in a rolled plate is shown in Fig. 64. In round or square bars, these bands become so many fibres whose size depends on the amount of reduction in cross sectional area from ingot to bar ; their effect on the properties of the material may or may not be noticeable, depending on circumstances. In flat bars, plates or sheets, however, they will produce a more or less laminated structure and this may have disconcerting effects where such a structure is a source of weakness.

As a spectacular, rather than an important, effect one may instance the oval appearance of the test pieces shown in Fig. 65. These were cut from flat bars of stainless iron containing about 15 per cent. chromium. Before testing, the cross section of each test piece was circular, and its oval shape after pulling appears to be due entirely to the remnants of the ingot structure being rolled out into tiny plates during the operations incidental to producing a flat bar. Similar but less noticeable effects may be produced in stainless irons containing 12/14 per cent. chromium when these are rolled or forged from high temperatures at which they consist, structurally, of mixtures of austenite and δ-iron, as described earlier. In the case of 12 per cent. chromium iron, no noticeable amount of δ-iron appears to be produced until the temperature exceeds about 1,200°C. ; when the chromium content reaches 14 per cent., the corresponding temperature is about 1,100°C.

The fact that the oval shape of the fractures in Fig. 65 is due to structural laminations in the steel may be shown by a simple and rather interesting experiment with ordinary mild steel. Two bars, 1⅜ inch square and 12 inches long, were cast in mild steel containing 0·31 per cent. carbon, 0·23 per cent. silicon and 0·57 per cent. manganese. One of these bars was reheated to 1,100/1,150°C. and then rolled down to a flat bar, ½ inch thick ; the other was similarly rolled but after reheating to a temperature of 700°C. only. Tensile test pieces prepared from these rolled bars, when pulled, had the fractures shown in Fig. 66. Piece A, from the bar rolled at 1,100°C. has a quite circular fracture ; that of piece B, rolled at 700°C., is oval. The explanation appears to be simple. The bars, as cast, had a coarse structure of

Plate XV
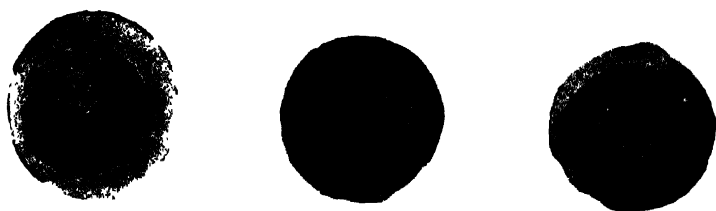
Fig 65   Oval fractures of tensile test pieces of stainless iron.

Fig. 66.   Circular and oval fractures of mild steel
test pieces rolled at 1150°C. and 700°C. respectively;
see page 88

ferrite and pearlite typical of a casting.   On reheating such material to 700°C., no diffusion of the ferrite and pearlite takes place and hence in the bar rolled at this temperature, these large grains are merely distorted, producing a laminated structure of the type found in stainless iron.   On the other hand, during reheating to 1,100/1,150°C., the large grains of ferrite and pearlite existing in the casting, are obliterated. The steel at this temperature consists of practically homogeneous austenite and hence on rolling, there is no production of the coarse laminated effect found in the bar rolled at 700°C., nor is there any tendency to ovalness in the tensile fracture obtained from the bar.

Like other things, however, which at first sight appear to be entirely objectionable, the extremely slow diffusion of the various elements present in stainless steel, which allows the original heterogeneity produced during solidification to be preserved to a greater or less degree, has some very distinct advantages for what may be described as instructional purposes. Thus it emphasises the fact, by making it more easily visible, that all forged or rolled steel, stainless or otherwise, possesses a " fibre " or " grain " which is quite as much a feature of steel as it is of wood, though it is not always so prominent to the eye in the metal.   This fibre is probably mainly due to the presence of minute particles of slag or other nonmetallic inclusions which are mixed up with the steel.   These, existing in the ingot as more or less rounded particles, are drawn out during forging or rolling operations into threads or plates, imparting to the worked product a fibre which should be taken into account quite as much as is the fibre in the working of wood.

Again, because the original crystalline characteristics of the ingot are not completely obliterated by heat treatment or by mechanical work, it follows that these characteristics can be recognised in the bars, forgings, stampings or other articles prepared from the ingot and thus help in correlating observed properties of the finished material or of its behaviour during hot working with ingot characteristics.   In the same way, the distortion of this original dendritic structure during forging operations produces a recognisable pattern in the forged article ; a study of this pattern often provides much useful information as to the methods of forging

employed. In these respects the behaviour of high chromium steel does not differ, except in degree, from that of ordinary steel or of the more common alloy steels. In all these steels the remnants of the ingot structure can be used in a similar manner ; in the high chromium steel, however, as with some other alloy steels, the lessened rate of diffusion of the carbon allows the original heterogeneity with respect to this element to persist in a marked degree and hence, reinforcing the effects of the differences due to other elements, enables the distorted ingot pattern to be more readily shown.

It may be noted, however, that one of the most useful elements to the steel metallurgist in disclosing ingot characteristics, sulphur, does not always function so well in this respect in high chromium steels. Sulphur exists in ordinary steels as minute particles of manganese sulphide, mechanically mixed with the steel ; a study of the distribution of these particles, easily carried out by means of a " sulphur print,"* gives much useful information as to ingot conditions. The possibility of obtaining such a print depends on the fact that the particles of manganese sulphide are easily attacked by dilute acids and the product of their decomposition reacts with the silver bromide in the photographic paper, producing a visible image. In many stainless steels, however, such amounts of sulphur as they contain exist in a different fashion ; the manganese content of such steels is generally low, e.g., not more than about 0·2 per cent. ; and under these conditions the sulphur appears to exist in a form, probably crystallised chromium sulphide, which is not readily attacked by acids and hence does not produce any " image " on the acidified bromide paper when the latter is pressed into contact with it. If, however, the manganese content of the steel is distinctly higher than suggested above, e.g., 0·6 per cent. or more, part at least of the sulphur then exists as manganese sulphide and from such steels a " sulphur print " may readily be obtained.

Thermal Curves. The absorption and evolution of heat occurring respectively at the Ac.1 and Ar.1 changes have long been used by metallurgists as a means of locating the

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* Such a print is obtained by pressing a piece of ordinary photographic " bromide " paper, previously soaked in water containing 2 or 3 per cent. of sulphuric acid, in contact with a smoothly filed or ground surface of the steel. Thirty to sixty seconds' contact is generally sufficient for ordinary steels. With stainless steel a stronger acid solution, up to about 10 per cent., may be used and a contact time of 5 to 10 minutes may be necessary.

Plate XVI
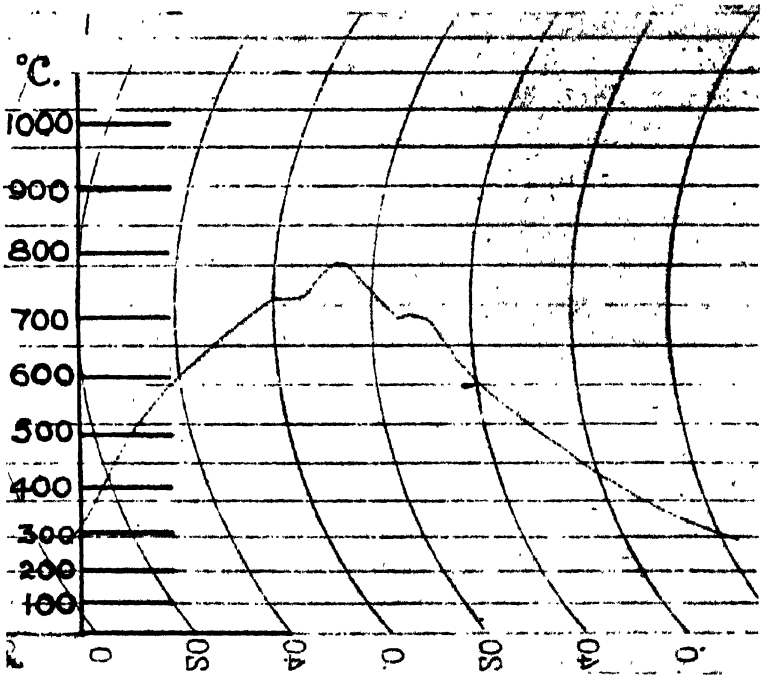
Fig. 67. Heating and cooling curves of ordinary tool steel obtained on works recorder.

exact temperatures at which these changes occur. They may be similarly used in connection with stainless steel, and a study of the results thereby obtained provides interesting and useful data in connection with the heat treatment of the steel.

Many elaborate forms of apparatus have been devised for the purpose of obtaining such thermal data on both ordinary carbon steels and alloy steels. For experimental work, where great accuracy in temperature measurement and the ability to detect minute changes in heat evolution or absorption are required, such elaboration of apparatus may be desirable ; for ordinary works purposes, however, an automatic temperature recorder, reading to five degrees centigrade, furnishes most, if not all, of the data required. Such a recorder gives a curve in which temperature is plotted against time. If such a recorder is connected to a thermocouple inserted in a hole drilled in a sample of steel and the latter placed in a furnace, the temperature of which is being raised at a uniform rate, the temperature of the sample will increase uniformly so long as no change takes place in the steel itself ; hence the curve drawn by the temperature recorder will be smooth and will show no perturbations. When, however, the Ac.1 point is reached, the change which then takes place absorbs a considerable amount of heat and hence, for a short interval, the steel either does not get any hotter or else increases in temperature at a slower rate than before, thus producing a break in the curve obtained from the temperature recorder. Similarly on cooling, the heat evolved by the steel on passing through the Ar.1 change temporarily delays the cooling of the sample until the change is completed. A record so obtained from a piece of ordinary carbon tool steel is shown in Fig. 67 and will serve as a standard with which the curves similarly obtained from stainless steel may be compared. It will be noted that the absorption and evolution of heat at Ac.1 and Ar.1 are both very sharply defined. A heating curve obtained in the same manner from a sample of stainless steel containing 0·3 per cent. carbon and 12·5 per cent. chromium gave the result shown in the left-hand portion of the curve in Fig. 68. In this case, the Ac.1 change occurs near 800°C., but otherwise the curve obtained is similar to that from the ordinary steel, except that the absorption of heat is possibly not so sharply defined but tends rather

to spread over a range of a few degrees than to occur at one temperature. This curve is typical of what may be obtained from stainless steel containing 0·3 per cent. carbon or thereabouts and chromium not exceeding about 15 per cent. ; the actual temperature obtained for the Ac.1 point with any particular specimen depends on the composition of the latter, more particularly with regard to silicon and nickel ; the former element raises the temperature of the Ac.1 change and the latter lowers it.

In addition, with any particular steel, the temperature at which the Ac.1 point occurs is affected slightly by the rate at which the sample is heated, a faster rate tending to give a somewhat higher temperature, and also by the previous thermal history of the sample. In the latter case, the Ac. 1 point is likely to occur a few degrees higher in a sample which has previously been annealed than in a piece of the same steel in the hardened or hardened and tempered conditions. This effect, which is probably connected with the relative sizes of the carbide particles given by the two types of heat treatment, may be seen in Fig. 68. Prior to taking the first heating curve in this diagram, the sample had been hardened and tempered ; after the subsequent slow cooling, producing the Ar.1 point at 760° C., the material was of course, in the annealed condition and in the second heating curve, which followed, the Ac.1 point occurred at 802° C. instead of 798° C.

In the case of the changes occurring on cooling, however, the rate at which the sample is cooled plays a very important part, as will be evident from what has already been stated when discussing the microstructural changes. The results obtained with the 12·5 per cent. chromium steel mentioned above may be summarised as follows : If the steel is cooled from above the Ac1. change point at a sufficiently slow rate to soften it completely (i.e., to give either a pearlitic structure similar to Figs. 2, 3 and 4, or the granular type, illustrated in Fig. 17, obtained under similar cooling conditions from temperatures at which all the carbide had not been taken completely into solution) an evolution of heat is produced in the range 770° to 700° C. approximately. The actual temperature at which this evolution of heat occurs depends on the rate of cooling employed and the maximum temperature to which the steel was heated before cooling.

Plate XVII
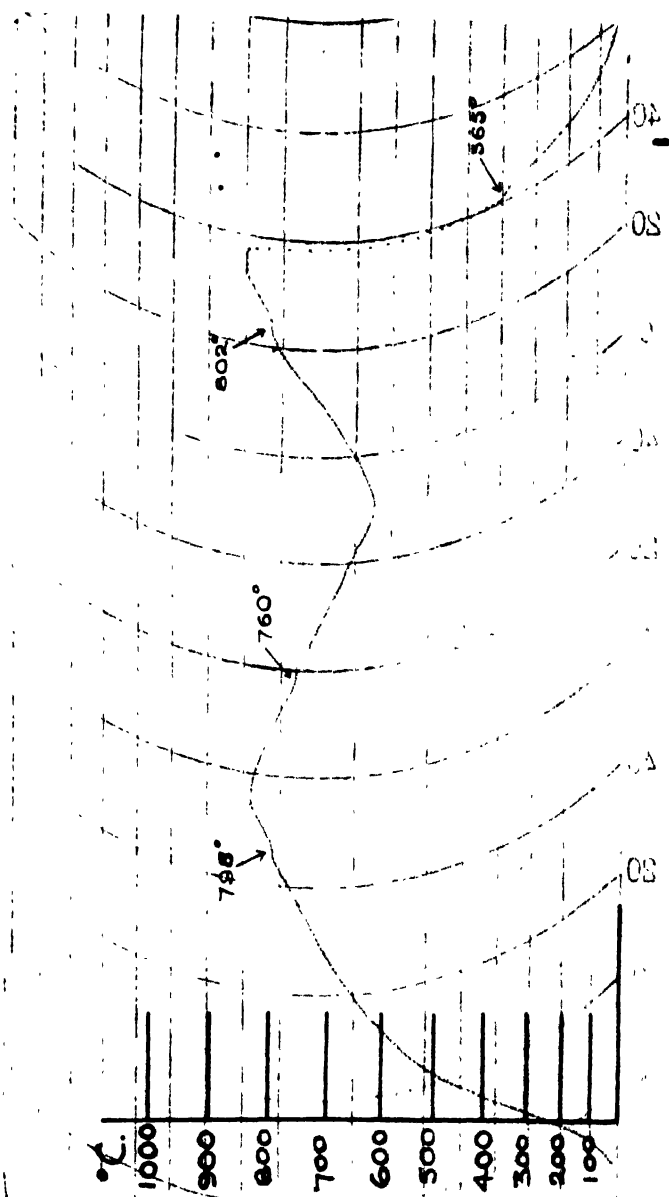
FIG. 68   Heating and cooling curves of stainless steel obtained on works recorder   (See page 92).

A slower rate of cooling tends to raise the temperature at which the change occurs, while raising the initial temperature from which the steel was cooled tends to lower the change point. It follows from this that the highest temperature at which the evolution of heat can occur is most likely to be obtained by heating the sample initially to a temperature only just above that of the change point on heating and then cooling slowly therefrom. Under such conditions, the evolution of heat is very well marked and occurs at about 760°C. or slightly higher. On increasing the rate of cooling, while still retaining the same initial temperature from which the cooling commenced, the temperature at which the evolution of heat occurs falls slightly, the critical change, however, being still well marked. This continues until a cooling rate fast enough to cause the steel to commence to harden is reached. The evolution of heat then becomes less defined and occupies a range of temperature while a further change occurring at about 400° C. becomes visible. With still faster rates of cooling, the upper change becomes less marked, and occurs at still lower temperatures, while the lower one becomes more marked. At the same time, the hardness of the samples after cooling increases rapidly. Finally, the upper change disappears entirely and there is obtained only the one occurring at about 350°/400° C.

As an illustration of this, the following table gives the results obtained on a steel containing :—

Carbon	...	0·34 per cent.
Silicon ...	...	0·12 per cent.
Manganese	...	0·24 per cent.
Chromium	...	11·2 per cent.

cooled at different rates from 860° C. The rates of cooling were measured by taking the time occupied in cooling from 850° to 550° C.

When samples are cooled from a higher initial temperature, a similar sequence is obtained except that the rates of cooling necessary to obtain similar effects become progressively slower as the initial temperature of cooling is raised. This will be apparent from Fig. 18 and the descriptions with regard to the structural changes which were given earlier in the chapter.

Time of Cooling.	Temperature of Critical Range.				Brinell Hardness Number After Cooling.
54 min.	766°	...	...	...	170
15 „	748° to 742° C. ...	...	...	...	179
13 „	741° to 735° C. ...	...	...	...	179
11 „	⎰ 720° to 700° C. ...⎱ 410° C.	...	...	...	255
9 „	⎰ 715° to 700° C. ...⎱ 385° C.	...	...	...	277
8½ „	⎰ 700° to 665° C. ...⎱ 385° C.	...	...	...	311
6½ „	⎰ Slight, between 700° and 600° C.⎱ 405° C.			...	382
3½ „	360° C. ...	...	...	...	387
1½ „	350° C. ...	...	...	...	402

The types of cooling curves obtainable on a works recorder are shown in Fig. 68; in the first cooling curve depicted therein, the sample was slowly cooled in the furnace and gave a well-defined Ar.1 point at 760°C. For the second cooling curve, the sample ($\frac{3}{4}$-in. diameter and 1-in. long) was withdrawn from the furnace at a temperature of 840°C. and allowed to cool freely in the air, producing the "lowered" Ar.1 point at 365° C.

The temperature at which the "lowered" Ar.1 point occurs, that is, the one obtained at 400°C. or below when the steel is cooled at a sufficiently fast rate to cause it to harden more or less completely, depends on the maximum temperature to which the steel was heated before cooling. The higher this maximum temperature is, the lower the position of the change point. Thus, in the examples quoted above, the lowered change point occurred between 350° and 400° C., the maximum temperature to which the steel was heated prior to cooling being 860° C. When the same steel was cooled from 1,200° C., the lowered change point occurred in the range 250° to 275° C.

The significance of the change points occurring in these two ranges of temperature, approximately 600° to 750° C. and 250° to 400° C., is readily apparent from a microscopical point of view. That occurring in the upper range marks the breakdown of the austenite with the formation of pearlite or of its finer varieties, sorbite and troostite. The lower

critical range, on the other hand, marks the formation of martensite from the austenite.   When the rate of cooling is such that evolutions of heat occur in both ranges of temperature, a structure consisting of a mixture of martensite and troostite is produced, the proportions of the two constituents depending on the relative amount of the heat evolutions in the two ranges of temperature.

Although the data given in the last few paragraphs refer more particularly to the type of stainless steel containing 11 to 14 or 15 per cent. chromium and about 0·3 per cent. or more carbon, they also apply, subject to certain modifications as regards temperatures, to all other stainless steels which are capable of being hardened by cooling more or less rapidly from high temperatures.   They also apply to the lower carbon stainless steels and irons containing up to about 14 or 15 per cent. chromium, except that the thermal effects in such alloys are less pronounced and hence less noticeable in thermal curves.

On the other hand, thermal curves obtained from the higher chromium stainless irons, containing more than about 15 or 16 per cent. chromium, show no noticeable evolutions or absorptions of heat, due to the fact that the changes which occur in such materials, on heating or cooling, take place so sluggishly and are spread over such a range of temperature that generally their rates of heating or cooling, when plotted, show no appreciable deviation from a smooth curve.   The determination of the structural changes taking place in such high chromium irons, and the temperatures at which they occur, is best performed by heating, for sufficiently long periods, small samples of the iron to various temperatures in the range in which structural changes are presumed to occur and then rapidly quenching them in water.   The quenched samples are then examined microscopically or submitted to such physical tests, e.g., hardness determinations, as may seem desirable.

Most of the austenitic stainless alloys to be described in subsequent chapters possess no change points on heating or cooling.   Such alterations in structure as may occur in them, are generally brought about by more or less prolonged soaking in certain ranges of temperature or, if produced more quickly, do not give rise to any appreciable evolution or absorption of heat.   Hence the thermal curves obtained from such alloys are perfectly smooth and show no evidence of internal structural changes.

MECHANICAL AND PHYSICAL PROPERTIES OF HIGH CHROMIUM STEELS

CHAPTER III

The suitability of any metal for engineering purposes is judged to a large extent by its properties as shown by the different types of mechanical tests which are in use for this purpose. As there appears to be a very large and promising field for the use of the various types of stainless steels for engineering work of many kinds, it is important that the range of mechanical properties obtainable from these steels should be studied in some detail.

Confining attention for the present to those stainless steels which depend solely on the presence of chromium for their distinguishing non-corrosive character, it will again be advantageous, as in the previous chapter, if consideration be given first to the properties of those steels which contain about 12 or 14 per cent. of this metal and afterwards to the modifications produced in these by the additions of still larger amounts of the alloy.

Experience has shown that in all types of hardenable steels, and particularly alloy steels, the best combinations of strength, ductility and toughness are obtained by first hardening the steel, so as to produce a homogeneous structure of martensite and then softening the hardened product, by tempering, so that the required tensile strength or hardness is obtained. In other words, what is aimed at, though possibly unconsciously, is the production of a structure in which there are no sharply defined constituents, such as the pearlite and free ferrite or cementite which are obtained by normalising ordinary carbon steels and such alloy steels as do not air harden or by annealing practically all steels ; but, on the contrary, one in which the carbide occurs in minute granules evenly distributed in a background of fine-grained ferrite. Actually much of the superiority of alloy steels is due to the fact that they can be completely hardened with

ease in bars or pieces of a size which by no practicable method of quenching could be hardened throughout, if made of ordinary carbon steel. Such hardened bars of alloy steel may then be tempered and, as a result, possess a high degree of uniformity of hardness, toughness and ductility from surface to centre. These good features are possessed by the hardenable stainless steels in common, with other alloy steels which air harden or oil harden with ease.

A considerable range of mechanical properties may be obtained from any one steel by varying the tempering temperature, after hardening ; the extent of this range may be indicated in a satisfactory and useful manner by suitably hardening a number of bars of the steel and then tempering individual bars at a series of gradually increasing tempering temperatures. The size of the bar chosen for such tests has often a very important bearing on the results obtainable from a given steel. The smaller the diameter of a bar, the more quickly it may be cooled and with a steel such as ordinary carbon steel, in which the rate of cooling necessary to harden the steel is comparatively fast, the amount of hardening obtained depends, in a very great degree, on the size of the bar used. Air hardening steels, and many types of stainless steels come in this category, harden at comparatively slow rates of cooling and therefore are not so susceptible to mass effects ; hence the results obtained from such steels , by using bars of small size, for example, one inch or so in diameter, can be applied to bars of considerably larger size. Most of the tests given in this and succeeding chapters were obtained on bars one inch to one-and-a-quarter inches diameter, but the results may be applied, with some limitations to be dealt with later, to bars five or six times that size. From the heat treated bars tensile test pieces were machined (British standard size, 2 in. by 0·564 in.) and also test pieces for the Izod impact test (10 mm. square test pieces, standard " Vee " notch), the latter test indicating the toughness of the material and being, in the author's opinion, of the greatest importance in judging the quality of steel for engineering purposes.

The results obtainable from stainless iron, containing about 12 per cent. chromium, after oil hardening and then tempering at various temperatures are illustrated in Table I. They are also plotted in Fig. 69, which enables the

variation of mechanical properties with tempering temperature to be visualised more readily.

For such very mild material as this, quenching in oil is sometimes preferable to air hardening, because the hardness obtained by air cooling is, generally speaking, somewhat lower than that by quenching in oil. The difference is probably due, not to the breakdown of the martensite during air cooling, but to the separation of ferrite, the latter being hindered by the more rapid cooling in oil.

The bars, when hardened, had a tensile strength of approximately 73 tons per square inch, and in this condition possessed good ductility and toughness. The effect of

TABLE I.

Mechanical Properties of Stainless Iron.

(Bars treated : 1⅛″ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·07	0·08	0·12	11·7	0·57

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.
*O.H. 980° C.	—	78·2	13·5	41·9	340	28
„ W.Q. 200° C.	—	73·0	12·0	38·0	340	84
„ „ 300° C.	—	72·4	12·5	36·4	332	88
„ „ 400° C.	—	72·8	15·5	51·0	332	38
„ „ 500° C.	58·8	72·4	18·0	52·2	340	86
„ „ 600° C.	38·0	49·1	22·0	62·4	241	65
„ „ 700° C.	30·6	40·4	26·5	65·8	196	79
„ „ 750° C.	27·9	36·4	31·0	68·8	179	87
„ „ 800° C.	33·6	53·6	13·5	44·6	255	40

* In the preparation of tables, the use of readily understandable abbreviations is often a matter of some convenience. The signs W.H., O.H., A.H., are easily apparent abbreviations for water, oil, and air hardening, respectively. With regard to tempering temperatures, it will be shown later that the speed of cooling after a tempering operation may have a distinct influence on the impact results obtained from a treated test piece. Test pieces are therefore generally quenched in water from the tempering heat and the expression W.Q. 600°C. indicates that a sample was so quenched from this tempering temperature. Similarly F.C. 600° C. and A.C. 600 ° C. indicate respectively cooling more or less slowly in a furnace and air cooling from the tempering heat.

tempering on the tensile strength was such as would be
expected from the Brinell hardness curves given in Fig. 18.
Up to a temperature of 500° C. the tensile strength was
practically unaffected by tempering while the toughness and
ductility were notably improved.   Between 500° and 600° C.
the tensile strength fell rapidly so that the bars tempered at
the latter temperature gave a figure of 49 tons per square inch.
Concurrently with this fall in tensile strength, there was a
distinct increase in the ductility figures (elongation and
reduction of area) and a still more marked increase in the
toughness value.   As the tempering temperature rose from
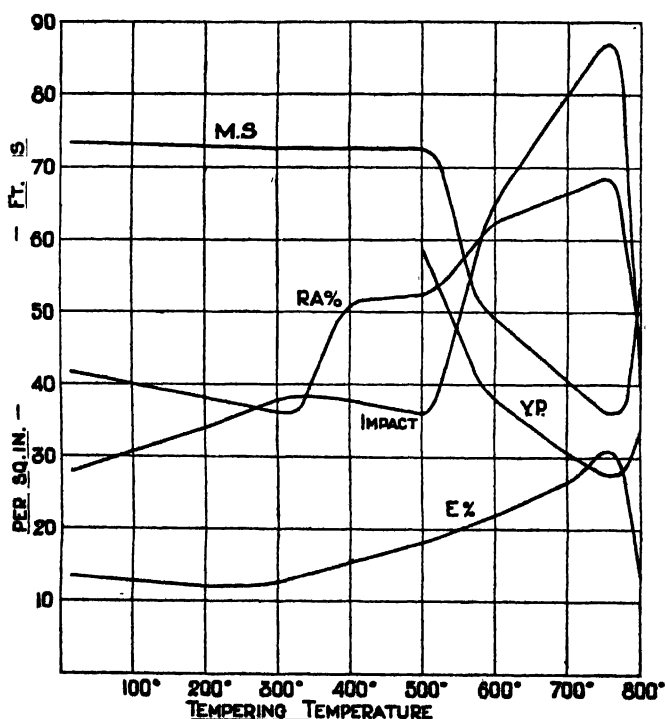
Fig. 69.   Mechanical properties of stainless iron, containing 0·07 per cent.
carbon and 11·7 per cent. chromium, after hardening and tempering.

600° to 750° C., the tensile strength fell steadily from 49 tons
per square inch to just under 37 tons per square inch, the
ductility figures at the same time increasing regularly.
In this steel, the carbon change point occurred between

790° and 800° C., and hence the bar tempered at 800° C. showed distinct hardening effects which were made more evident owing to the bars being quenched in water from the tempering heats.

It may be of interest to note that the results given above were obtained from the first cast of stainless iron produced on a commercial scale and which was referred to on page 28.

TABLE II

Mechanical Properties of Stainless Iron.
(Bars treated: 1⅛" diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·10	0·46	0·31	11·2	0·44

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.		
A.H. 950° C.	69·2	78·0	12·0	36·4	302	18	20	20
O.H. 950° C.	—	84·7	8·0	8·4	340	20	31	28
„ W.Q. 500° C.	—	82·6	18·5	57·0	340	19	18	18
„ „ 600° C.	46·0	55·0	22·0	63·7	241	24	29	—
„ „ 700° C.	36·0	43·6	27·0	66·8	192	120	120	120
„ „ 750° C.	32·7	40·8	32·0	67·0	179	120	120	120
„ „ 800° C.	28·8	39·6	32·5	65·8	170	109	110	105

Results similarly obtained on a sample with somewhat higher carbon content but otherwise similar in analysis are given in Table II and plotted in Fig. 70. In this case the material when hardened had a tensile strength of 85 tons per square inch, and after fully tempering, at 750° to 800°C., a value of about 40 tons per square inch was obtained. A test after air hardening is also given and illustrates the somewhat lower tonnage obtained by air cooling as compared with oil quenching. In many cases, however, and especially if the bars are afterwards fully tempered, the difference between the properties of air hardened and oil hardened bars of this material is negligible.

Similar results may be obtained from irons containing rather more chromium, i.e., 18/14 per cent., though these irons, other things being equal, do not harden quite so intensely as those containing 12 per cent. or so. 950°C. is
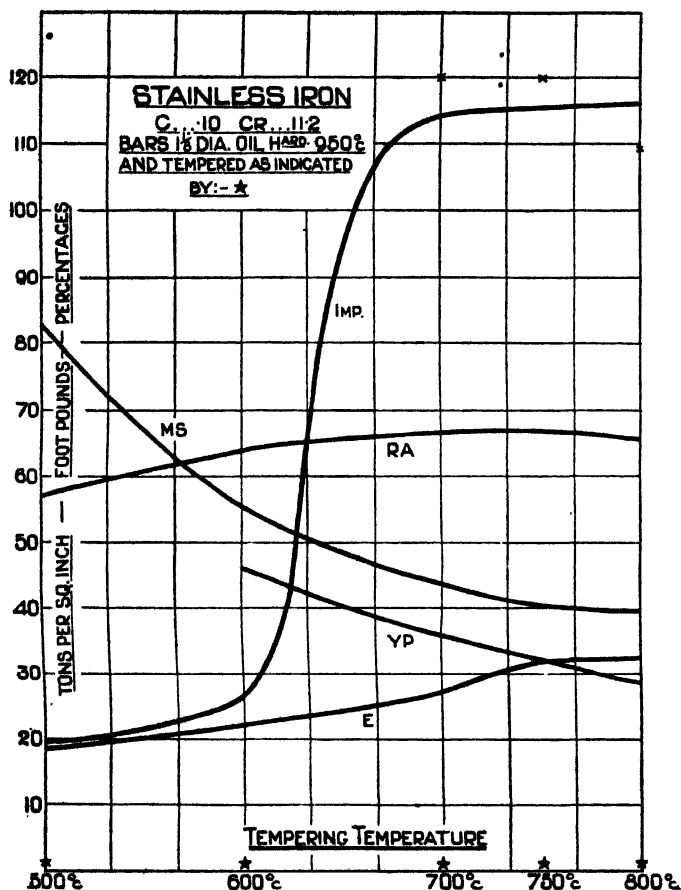
FIG. 70. Mechanical properties of stainless iron, containing 0·10 per cent. carbon and 11·2 per cent. chromium, after hardening and tempering.

a suitable hardening temperature and the results given in Table III are typical. The comparatively low tensile strength of the air hardened bar should be noted.

Stainless iron of a composition similar to this finds many applications in engineering work. It possesses a very useful range of mechanical properties and, as will be seen

Table III

Mechanical Properties of Stainless Iron.
(Bars treated : 1″ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel ‰
0·07	0·32	0·29	13·3	0·40

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.	
A.H. 950° C.	26·5	49·8	23·0	53·4	228	40	30
O.H. 950° C.	58·8	69·6	18·5	51·0	321	11	12
,, W.Q. 500° C.	56·4	68·0	21·5	61·5	302	13	—
,, ,, 600° C.	35·2	45·6	25·5	71·8	207	91	92
,, ,, 750° C.	26·6	38·6	34·0	68·8	179	110	110

Table IV

Mechanical Properties of Mild Stainless Steel.
(Bars treated : 1⅛″ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·16	0·52	0·27	13·0	0·31

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.		
OH. 950° C.	89·6	94·4	7·0	11·8	444	42	38	28
,, W.Q. 500° C.	84·0	94·0	20·0	59·3	444	22	27	18
,, ,, 600° C.	44·0	54·8	24·5	64·8	255	47	64	40
,, ,, 650° C.	38·8	48·4	24·0	66·8	241	87	93	88
,, ,, 700° C.	37·2	44·8	28·5	70·8	217	101	101	99
,, ,, 750° C.	36·8	43·4	31·0	66·8	202	120	120	120

later, adequate resistance to corrosion for many purposes ; the fact that it does not air harden to the same extent as irons of lower chromium content, e.g., 11/12 per cent., is frequently an advantage in connection with its engineering application.

Raising the carbon content of the stainless steel produces effects similar to those obtained under the same circumstances in ordinary carbon steels. The tensile strength of the steel, under given conditions of heat treatment, gradually rises while the toughness and ductility figures become less. The curves connecting these properties with tempering temperature are however of the same type as those for the

TABLE V

Mechanical Properties of Mild Stainless Steel.
(Bars treated : 1⅛″ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·16	0·28	0·20	13·0	0·51

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.		
A.H. 950°C. W.Q. 300°C.	—	88·5	10·5	32·9	402	36	35	—
,, ,, 600°C.	44·8	54·8	23·0	60·4	262	75	81	80
,, ,, 650°C.	40·0	48·0	24·0	62·2	241	93	100	102
,, ,, 700°C.	39·3	46·2	26·0	62·2	217	95	101	91
,, ,, 750°C.	34·4	44·2	31·0	65·8	207	95	92	93

lower carbon irons. Steels with a carbon content between 0·15 and 0·25 per cent. are very well adapted for many engineering purposes where a somewhat higher tensile strength than that given by stainless iron is required. Here again there is some difference, in air hardening capacity, between chromium contents of about 12 and 14 per cent., but it is less noticeable than in stainless iron. Tables IV to VII and Fig. 71 indicate the type of result to be expected from material in this range of carbon content. One may note the useful combinations of tensile strength and toughness, which such steels possess ; also, when hardened, followed or not by tempering up to 500°C., they are generally sufficiently hard (Brinell hardness number 300 to 450 depending on composition) to serve for many purposes where a surface to resist erosion or wear is required.

When the carbon content rises over about 0·30 per cent.,

the steel becomes hypereutectoid and hence more in the nature of a tool steel than a constructional steel. Such steels when hardened give higher Brinell hardness numbers than those with lower carbon and they are not softened, by tempering, below a tensile strength of 50 to 55 tons per square inch. Increase in carbon content over this amount has not such a

TABLE VI.

Mechanical Properties of Mild Stainless Steel.

(Bars treated : 1⅛″ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·22	0·11	0·17	11·5	0·76

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Izod Impact, ft. lbs.		
O.H. 900° C. W.Q. 500° C. ...	84·4	88·0	9·5	86·4	15	14	18
,, ,, 600° C. ...	42·0	56·4	24·0	52·2	25	23	—
,, ,, 700° C. ...	88·0	46·8	26·0	58·0	60	60	67
,, ,, 750° C. ...	31·2	43·9	28·0	61·5	68	68	70

TABLE VII

Mechanical Properties of Mild Stainless Steel.

(Bars treated : 1⅛″ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·22	0·18	0·14	18·0	0·60

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.		
A.H. 950° C. W.Q. 800° C.	—	—	—	—	444	11	12	15
,, ,, 600° C.	55·0	66·6	17·0	48·5	311	11	11	12
,, ,, 650° C.	51·0	*60·6	18·0	51·0	277	15	15	15
,, ,, 700° C.	48·4	51·6	27·0	57·0	255	61	61	50

noticeable effect on the mechanical properties obtainable under given conditions of treatment as it has in the lower ranges of carbon, nor is the effect of a variation in chromium content between 12 and 14 per cent. so marked. The properties obtainable are illustrated by the results given in Tables VIII and XI, which refer to steels containing 0·37 and 0·50 per cent. carbon respectively and which also show that such steels when suitably heat treated are quite tough and ductile.
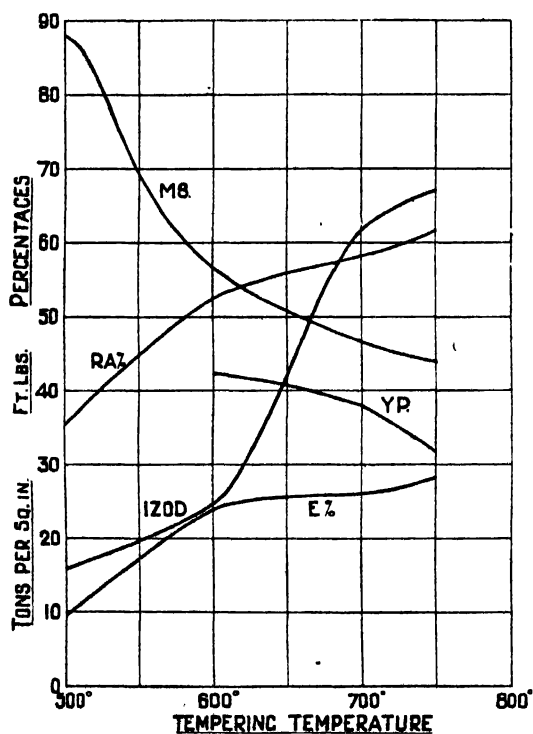
Fig. 71. Mechanical properties of stainless steel, containing 0·22 per cent. carbon and 11·5 per cent. chromium, after hardening and tempering.

With a still higher carbon content than this, the material contains very large amounts of free carbide ; as an indication however, of the type of mechanical properties possessed by such steels, the results given in Table X are included. They are interesting also in that they confirm what was said earlier, that the effect of increasing carbon content on the

TABLE VIII.

Mechanical Properties of Hard Stainless Steel.

(Bars treated : 1⅛″ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %
0·37	0·19	0·15	11·7

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.		
A.H. 900° C.	—	102·0	3·0	3·2	444	5	8	8
„ W.Q. 300° C.	—	100·0	5·5	6·7	444	5	5	5
„ „ 500° C.	—	104·4	9·0	24·6	444	8	4	—
„ „ 550° C.	—	91·2	9·0	80·6	487	11	11	7
„ „ 600° C.	57·8	65·0	11·5	27·6	302	7	10	7
„ „ 650° C.	50·2	56·4	17·5	87·8	269	15	10	15
„ „ 700° C.	46·8	54·0	21·0	52·2	241	26	26	21
„ „ 750° C.	42·4	51·8	21·0	44·6	241	28	33	84

TABLE IX.

Mechanical Properties of Hard Stainless Steel.

(Bars treated : 1⅛″ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %
0·50	0·14	0·13	12·2

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.		
A.H. 900° C.	—	—	—	—	477	4	5	4
„ „ W.Q. 300° C.	—	—	—	—	444	6	4	5
„ „ „ 400° C.	—	108·2	7·5	11·8	444	6	5	6
„ „ „ 500° C.	—	98·2	6·0	21·4	415	8	8	4
„ „ „ 600° C.	55·6	62·0	15·0	42·0	285	18	18	14
„ „ „ 650° C.	50·2	56·8	18·0	45·9	262	12	12	18
„ „ „ 700° C.	46·4	53·6	20·0	49·7	241	24	25	25
„ „ „ 750° C.	42·6	51·4	28·0	52·2	245	30	30	80

mechanical properties of these high carbon steels, under given conditions of heat treatment, is not nearly so marked as it is with steels of lower carbon content.

<div align="center">TABLE X.</div>

<div align="center">• <i>Mechanical Properties of High Carbon Steels.</i></div>

<div align="center">ANALYSIS.</div>

No.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
1	0·96	0·17	0·33	13·1	0·45
2	1·08	0·17	0·34	13·1	0·50
8	1·18	0·10	0·29	13·1	0·45
4	1·42	0·12	0·35	13·1	0·44

<div align="center">TESTS (Bars treated : 1¼″ diameter.)</div>

No.	Treatment.		Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.		
1	A.H. 900° C.	W.Q. 650° C.	30·0	59·0	10·0	18·3	265	9	8	8
	,,	,, 700° C.	85·6	53·8	18·5	36·4	255	7	7	10°
	,,	,, 750° C.	41·2	53·5	19·0	39·2	241	14	13	17
2	A.H. 900° C.	W.Q. 650° C.	44·4	62·4	7·0	10·1	285	11	9	22
	,,	,, 700° C.	38·0	56·6	17·5	29·1	277	17	16	21
	,,	,, 750° C.	44·0	57·8	14·5	29·1	265	18	9	15
8	A.H. 900° C.	W.Q. 650° C.	40·8	61·6	8·0	11·8	285	15	17	—
	,,	,, 700° C.	40·8	58·2	15·5	30·6	277	17	11	—
	,,	,, 750° C.	30·0	56·8	15·0	26·1	265	15	10	16
4	A.H. 900° C.	W.Q. 650° C.	38·0	61·9	7·0	13·4	302	11	5	5
	,,	,, 700° C.	40·8	59·7	10·0	18·8	285	8	8	—
	,,	,, 750° C.	38·6	58·9	10·0	18·8	281	5	14	5

Hardening Temperature. It will be noticed from the diagrams and figures given that the hardening temperatures required for stainless steels of the type described varies somewhat with the carbon and chromium contents of the material to be treated. For the mildest steels or stainless irons, and also those of somewhat higher carbon content, i.e., 0·15 to 0·20 per cent., air cooling or oil quenching from 950°C. provides a suitable method. At about 0·25 per cent. carbon, .

the temperature may with advantage be dropped to 925°C. and to 900°C. with 0·3 per cent. carbon and upwards if the chromium content is in the neighbourhood of 12 per cent. When the latter is raised to 14 per cent. or thereabouts, it may be advantageous to adopt 950°C. for all carbon contents, owing to the general action of chromium in raising the Ac.1 point and retarding the solution of the carbide in the steel.

The effect of varying hardening temperature on the resistance to corrosion will be dealt with in a later chapter, but the effect on the mechanical properties of increasing the hardening temperature may be briefly dealt with here.

In Chapter II, the progressive solution of the carbide in the steel, as the latter is heated through the range of a hundred and fifty degrees or so above the Ac.1 point, was described, and also its effect on the hardness of samples quenched in this range. Owing probably to this gradual solution of the carbide, the air hardening capacity of the steel also increases as the temperature, from which air cooling takes place, rises through the same range. The solution of the additional carbide appears also to increase the tensile strength of the steel after tempering at a given temperature so that if bars of the same steel are hardened, for example, at 900°, 950°, and 1,000°C., not only would the samples hardened at the higher temperatures be somewhat harder than those hardened at the lower temperatures (and also, incidentally, would harden at slower rates of cooling) but in addition, if the samples so treated were tempered together at, for example, 700° C., the one hardened at 900° C. would have the lowest and that hardened at 1,000° C. the highest hardness and tensile strength. The greater hardness obtained, after tempering, from samples quenched at higher temperatures was noted in connection with high carbon steel (page 58, and Fig. 88) and is also illustrated by the curves in Fig. 72, in which are plotted the Brinell hardness numbers obtained from samples of a steel containing

Carbon	......	0·82 per cent.
Silicon	......	0·26 per cent.
Manganese		0·29 per cent.
Chromium		12·2 per cent.
Nickel	....	0·85 per cent.

which had been oil quenched from 900° and 1,050° C.

respectively. In all cases, the samples quenched at high and low temperatures were tempered together in the same furnace. It will be seen that the hardness of the samples
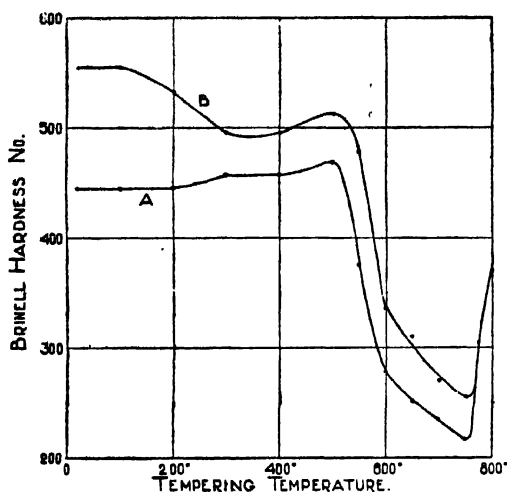
Fig. 72. Effect of hardening temperature on the subsequent tempering of stainless steel (0·32 per cent. carbon and 12·2 per cent. chromium).

Curve A. Hardened at 900°C.
Curve B.   „   „ 1,050°C.

TABLE XI.

Effect of Hardening Temperature on Hardness and Toughness of Stainless Steel.

(Bars treated : 1¼″ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·25	0·18	0·22	12·5	0·21

Treatment.	Brinell Hardness No.		Calculated Maximum Stress, tons per sq. in.	Izod Impact, ft. lbs.
	After Hardening.	After Tempering.		
A.H. 900° C. W.Q. 700° C.	480	228	50	85 86 80
A.H. 950° C. „	477	241	52	47 67 71
A.H. 1,000° C. „	582	248	54	86 85 85

quenched from the higher temperature remains steadily above that of the other samples until the tempering temperature reaches the Ac.1 point.

The influence of the hardening temperature on the mechanical properties is also illustrated by the figures given in Table XI, which show, in addition, that the increased hardness produced by the higher quenching temperature is accompanied by a notable decrease in toughness. This, of course, is in line with what occurs with other types of steel.

Similar results are obtainable from even the low carbon stainless irons, though in this case, the drop in toughness may not be so noticeable. It is quite perceptible, however, with a steel containing 0·16 per cent. carbon as will be seen from the figures given in Table XII.

TABLE XII.

Effect of Hardening Temperature on the Hardness and Toughness of Mild Stainless Steel.

(Bar treated : 1⅛″ diameter)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·16	0·52	0·27	13·0	0·31

Treatment	Yield Point, tons per sq. inch	Max. Stress, tons per sq. inch	Elonga-tion % on 2 ins	Reduc-tion of Area %	Brinell Hardness No. Hard'd.	Brinell Hardness No. Temp'd	Izod Impact, ft. lbs.		
O.H. 900° W.Q. 750° C.	34·0	44·2	33·0	67·8	336	196	110	111	110
O.H. 950° „	40·8	47·8	28·0	65·8	402	217	95	108	93
O.H. 1,000° „	42·0	49·1	25·0	63·6	444	235	82	93	95

These two tables illustrate the effect of raising the hardening temperature above that generally employed. On the other hand, if a lower temperature than this be used, but one still above that at which the Ac.1 change occurs, effects more or less opposite in character are produced. The steel hardens to a limited extent only and on subsequent tempering, e.g., at 700°C., becomes softer than it would have been if hardened effectively prior to

tempering. The effects of using such a low hardening temperature are illustrated in Table XIII. Although such a procedure is not to be recommended as a final heat treatment operation (the mechanical properties of any steel, when it has been only partially hardened before tempering are not so good as if it had been fully hardened), it may have obvious advantages as an intermediate treatment, e.g., during cold working operations or before machining, when a softer material than that ordinarily obtained either by hardening and tempering or by simply tempering a rolled bar or forging is desirable, and annealing (see page 115) is not convenient. In such cases, the low yield point of the material treated in this manner is advantageous.

TABLE XIII.

Effect of Partial Hardening on the Hardness of Tempered Stainless Steel.

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·22	0·13	0·14	13·0	0·60

Rolled Bar (1⅛″ diameter). Brinell Hardness No., as rolled, 555.

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness No. Hard'd.	Brinell Hardness No. Temp'd.	Izod Impact, ft. lbs.
W.Q. 700° C.	47·0	53·8	21·0	54·6	—	255	54 53 52
A.H. 950° W.Q. 700° C.	46·3	50·1	23·0	54·6	477	241	56 56 53
A.H. 850° ,,	22·0	45·7	27·5	63·6	269	212	69 67 63

Effect of Size of Bar on Impact Tests. It was stated on page 100 that the results of mechanical tests obtained on bars of stainless material of about one inch diameter could be applied with certain restrictions, to bars five or six times that size. With regard to the tensile tests, the results on the larger bars will be very similar to those on the one inch bars except that, under similar conditions of treatment, slightly lower values of the tensile strength may be obtained from the larger bars. The impact values obtained, however, tend to fall off when the size of bar exceeds two or

three inches diameter. As an illustration, the following results obtained on steel of the following analysis :—

Carbon ...	...	0·30 per cent.
Silicon	..:	0·17 per cent.
Manganese	...	0·23 per cent.
Chromium	...	12·4 per cent.
Nickel ...	...	0·55 per cent.

may be quoted. Test A was obtained from a bar 1¼ inches diameter, while test B was taken from another, 4 inches diameter, made from the same 12 inch square ingot. The heat treatment (O.H. 900°C., W.Q. 700°C.) was the same in each case.

	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.
A (1¼″ diameter) ...	39·4	51·6	24·0	59·8	241	73 65 —
B. (4″ diameter) ...	39·0	51·0	25·5	57·0	241	87 34 31

The effect is due not so much to the difference in size of the pieces during the heat-treatment operation but probably to the fact that the larger bar has had less mechanical work during its manufacture.

From an examination of all the results of the mechanical tests which have been given it will be evident that the properties of the type of stainless steel under discussion compare very favourably with those of the very highest qualities of structural alloy steels. It will also be evident that the range of hardness and tensile strength available is ample for most engineering purposes.

Tests on Annealed Material. It has been pointed out earlier that the slow cooling of stainless steels, from temperatures above the carbon change point, produces structural results comparable with those obtained by the normalising, or slower cooling, of carbon steels. The mechanical properties of such annealed stainless material are also similar to those of normalised carbon steel and are characterised, when compared with the tests obtained from the same material when hardened and tempered, by low values of tensile strength and yield point, the fall in the latter

being especially marked. The toughness and ductility values of annealed stainless steels depend to a very great extent on the temperature used for annealing.

The influence of annealing temperature on the microstructure of the annealed sample was pointed out on page 48. The two types of structure referred to as " pearlitic " and " globular," obtained by annealing respectively at temperatures high enough to dissolve the whole of the carbide and in the range of temperature above Ac.1 in which the carbide is not wholly dissolved, are so widely different that it would be expected the mechanical properties given by any one steel would vary with the type of structure obtained. The results obtained on a series of steels of differing carbon content after annealing at 880° and at 1,050° C., respectively are given in Table XIV.

TABLE XIV.

Mechanical Properties of Annealed Stainless Steel.

Composition.		Treatment.	Yield Point, tons per sq. inch	Max. Stress, tons per sq. inch	Elonga- tion % on 2 ins.	Reduc- tion of Area %	Brinell Hard- ness No.	Izod Impact, ft. lbs.
Car- bon. %	Chro- mium. %							
0·10	11·9	Annealed 880° C.	16·6	29·8	37·0	67·8	137	71 96 73
		Annealed 1,050° C.	22·0	30·3	40·0	73·6	137	39 41 20
0·14	11·6	Annealed 880° C.	17·2	35·8	34·0	65·8	163	27 27 27
		Annealed 1,050° C.	22·4	37·1	27·5	55·8	170	15 15 —
0·25	12·5	Annealed 880° C.	19·0	38·6	32·0	69·8	179	40 26 —
		Annealed 1,050° C.	22·0	41·3	26·0	47·2	192	8 5 8
0·32	12·7	Annealed 880° C.	18·4	41·1	29·0	65·8	179	23 15 —
		Annealed 1,050° C.	22·0	·45·6	24·0	44·6	202	3 3 —

These results show the gradual increase in tensile strength and hardness accompanying an increase in carbon content. They also bring out very clearly the difference in the mechanical properties associated with the globular and pearlitic types of structure. This difference is least with the lowest carbon content, though one may note the big drop in the toughness value of this steel brought about by annealing at the high temperature. With the higher carbon steels, the differences are more marked and one may especially note the higher tensile strengths of the pearlitic samples and

their very low toughness values. One may also observe that the samples annealed at 880° C. are not particularly tough when compared with the results obtained by hardening and tempering, especially if the low tensile strength of the annealed samples be taken into account.

Temper Brittleness. It is well known to makers and users of nickel chromium steels, and to a less extent of nickel steels, that there are certain limitations which have to be observed in the tempering of such steels if maximum toughness, consistent with required tensile strength, is to be obtained from them. Thus it is found that if samples of a nickel chromium steel are hardened and then tempered at successively higher temperatures, the toughness value does not increase uniformly with the tempering temperature. A sample tempered at 200° C. will be noticeably tougher than the untempered steel, but one tempered at 300° C. will be distinctly less tough than that tempered at 200° C. and probably less tough even than the untempered steel. Further, with increasing tempering temperature above 300° C., the toughness value only rises slowly until about 550° C., after which it rises sharply. Moreover, the toughness of samples tempered at higher temperatures, e.g., 600° or 650° C., depends to a large extent on the rate at which they are cooled after tempering. If quenched from the tempering heat they give a fine grey fracture and a high impact value; on the other hand, if slowly cooled, they give a crystalline fracture and a low impact value, although the tensile strength may be the same in both cases. The difference in impact value is often very large, thus the figure from the rapidly cooled sample may be ten or twenty times the value from the slowly cooled piece.

These characteristics are found in some degree in other alloy steels (though generally to a less marked extent than in nickel chromium steels) and they may also be produced in carbon steels. It is important, therefore, to see to what extent they are found in stainless steels. As in these steels, the actual tempering temperatures used to obtain given effects differ from those in ordinary nickel and nickel chromium steels, the question may be explored under two heads :—

(a) In the range up to 500° C., in which the tensile strength does not materially alter, does the impact value

increase regularly or is there any intermediate maximum value ?

(b) Does the rate of cooling of samples tempered at 600° C., or above, alter the impact value obtained ?

With regard to (a) it may be said definitely that the impact value does not generally increase uniformly with tempering temperature. Most samples give a maximum impact value when tempered between 200° and 400° C., so that increasing the temperature up to 500°C. tends to lower this value. There is, however, not the same regular variation in the impact value among different casts of stainless steel as there is, for example, with nickel chromium steels tempered at 200° and 800°C. Practically every piece of nickel chrome steel will show a drop in impact value after tempering at 800°C. In the case of stainless steel, some casts show a distinct drop in impact value when the tempering temperature is raised from 400° C. to 500° C., while with others, the toughness remains constant or even increases. Speaking generally, however, tempering in the range 200° to 400°C. is more likely to give maximum toughness for hardened material than tempering at 500° C., and, as a general working temperature, 800° C. would probably be suitable. Figs. 73 and 74 show the results obtained from a variety of stainless steels and indicate the type of results obtained on tempering in this range.

The other phase of temper brittleness, as set out in

TABLE XV.

Effect of Rate of Cooling after Tempering on Impact Value.

Cast.	How Cooled.				Brinell Hardness No.	Izod Impact, ft. lbs.		
R. 1,051	Quickly	...	...	...	251	45	45	—
	Slowly	...	...	...	251	22	21	20
R. 1,057	Quickly	...	...	...	241-	44	88	88
	Slowly	...	...	...	285	25	28	25
R. 1,069	Quickly	...	...	...	255	85	88	80
	Slowly	...	...	...	248	19	19	19
R. 1,081	Quickly	...	...	...	258	47	44	88
	Slowly	...	...	...	255	87	88	80
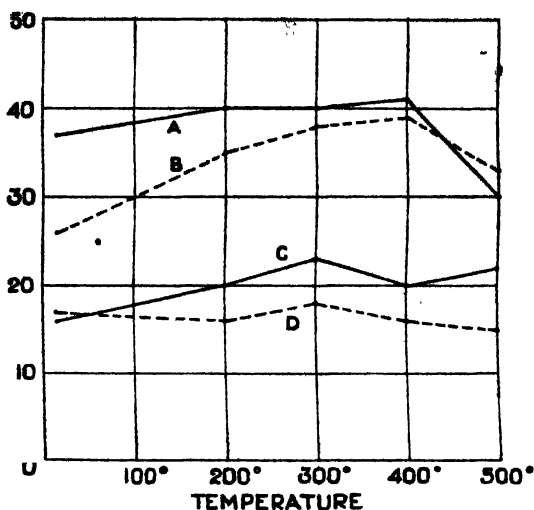
Fig. 73.   Impact values obtained from hardened stainless steels after tempering up to 500°C. :—

Curve.	Carbon, %	Chromium, %	How Hardened.	Average Brinell Hardness No.
A.	0·09	11·3	O.H. 950°	375
B.	0·16	13·0	O.H. 953°	430
C.	0·17	14·4	O.H. 950°	410
D.	0·23	12·8	A.H. 950°	437
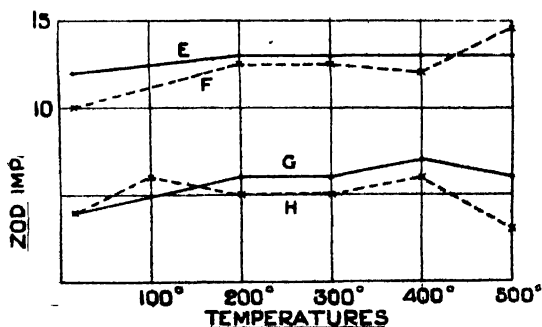
Fig. 74.   Impact values obtained from hardened stainless steels after tempering up to 500°C.:—

Curve.	Carbon, %	Chromium, %	How Hardened.	Average Brinell Hardness No.
E.	0·28	11·7	A.H. 900°	444
F.	0·29	11·7	A.H. 950°	444
G.	0·32	11·2	A.H. 900°	444
H.	0·50	12·2	A.H. 900°	477

paragraph (b), page 118, is also found in stainless steel, though
to a less degree than in nickel chromium steels.   Thus the
results given in Table XV were obtained on four casts of
stainless steel containing 0·30 to 0·31 per cent. carbon.   The
samples were air hardened from 900°C., and then tempered
at 700°C.   The quickly cooled samples were quenched in
water while the others were slowly cooled in a furnace, the
time taken to cool to 400°C. being 10 to 12 hours.

A noticeable feature of the temper brittleness found in
nickel chromium steels is that the susceptibility of different
casts to the effect of rate of cooling after tempering varies
considerably.   Some casts very easily become brittle while
other casts of the same chemical composition can be cooled
at comparatively slow rates and still retain their toughness.
A similar remark applies to stainless material ; some casts
of the steel are more susceptible than others.   Thus each of
the two casts of steel on which tests are given in Table XVI,

TABLE XVI.

Cast.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A.	0·25	0·21	0·22	12·2	0·20
B.	0·25	0·18	0·22	12·5	0·21

	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact., ft. lbs.
A. A.H. 925° W.Q. 700° C.	43·6	58·5	22·5	60·4	248	82 78 75
„ A.C. 700° C.	—	—	—	—	241	45 45 51
B. A.H. 925° W.Q. 700° C.	45·6	52·6	27·0	60·4	241	64 66 63
„ A.C. 700° C.	—	—	—	—	255	64 62 68

when quenched in water after tempering, gave very high
impact values as shown.   With the slower rate of cooling
obtained by allowing the bars (which were 1½ ins. diameter)
to cool freely in the air from the tempering temperature,
the impact value of one was lowered appreciably while the
other was quite unaffected.

It will thus be seen that the temper brittleness found in
stainless steels has the same peculiarities as that found in

nickel chromium steels and, as with the latter steels, although the precautions necessary to avoid its ill effects are known and can be applied to the various products, the actual cause of the brittleness is still unknown.

High Chromium Irons and Steels. The lessened hardening capacity of the stainless irons containing more than about 14 per cent. chromium has already been described in the preceding chapter ; as a consequence of this lessened capacity, the tensile strength obtained after hardening and tempering such material is not so high as with the lower chromium irons ; also, probably for the same reason, the high chromium irons have a lower ratio of yield point to maximum stress than those with less chromium, the values

TABLE XVII.

Mechanical Properties of High Chromium Irons.

(Bars 1⅛ inch diameter, hardened and tempered.)

Carbon %	Chromium %	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Izod Impact, ft.	lbs.	
0·08	14·3	24·0	37·2	32·5	67·8	90	89	93
0·10	14·4	29·6	37·2	33·0	69·8	100	97	97
0·07	14·9	28·8	35·8	34·0	67·8	75	65	78
0·14	15·2	19·4	34·5	34·0	67·8	73	59	65
0·10	15·4	22·0	31·4	40·0	73·6	4	5	4
0·09	15·5	18·0	31·8	36·5	65·8	85	62	86
0·09	15·5	22·9	32·4	38·0	70·8	9	11	9
0·17	15·9	26·0	36·8	34·0	62·6	65	65	73
0·07	16·0	23·6	35·8	31·0	61·5	35	25	30
0·09	16·1	18·0	29·8	39·0	69·8	15	13	—
0·11	17·1	20·8	30·2	38·0	67·8	4	4	5
0·10	17·9	18·0	27·8	40·5	66·8	3	3	3
0·10	20·4	18·4	27·9	34·0	49·7	3	2	3
0·09	22·8	20·4	28·2	21·0	26·1	3	3	8

obtained being similar to those of the annealed forms of the latter material. Typical properties are indicated in the tests given in Table XVII and these show that with a chromium content up to about 15 per cent., very tough, ductile material is obtainable. If more chromium than this is present however, the irons no longer possess the property

of great toughness, which is so characteristic of the lower chromium irons ; individual casts containing between about 15 and 16 per cent. may be satisfactorily tough, as is shown by some of the tests in Table XVII, but more often than not the material possesses an Izod value of only a few foot-pounds, no matter how it be heat treated.

As a further consequence of their lack of hardening power, it is not possible to vary their tensile strength to any extent by heat treatment ; this is illustrated by the tests given in Tables XVIII and XIX.   It is generally advisable, however, to temper these irons at 700° C., or thereabouts, after they have been air-cooled or quenched, from high temperatures, e.g., after ordinary forging or rolling operations, because the untempered material may be noticeably deficient in ductility and even less tough than usual.

TABLE XVIII.

Mechanical Properties of High Chromium Iron.

(Bars treated : 1⅛″ diameter).

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·09	0·36	0·22	15·5	0·39

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.		
A.H. 950° C.	27·2	34·8	29·5	55·8	179	7	4	6
,, W.Q. 500° C.	26·4	35·2	34·0	57·0	187	7	4	5
,, ,, 600° C.	24·0	32·4	35·0	71·8	166	7	7	7
,, ,, 700° C.	22·9	32·4	38·0	70·8	153	9	11	9
,, ,, 800° C.	22·0	30·4	41·0	73·6	149	5	4	3

The tests in Tables XVIII and XIX show that the characteristic features of these very high chromium irons are low tensile strength and yield point and very low Izod values.   The first two may be raised, as in other metals, by

Plate XVIII
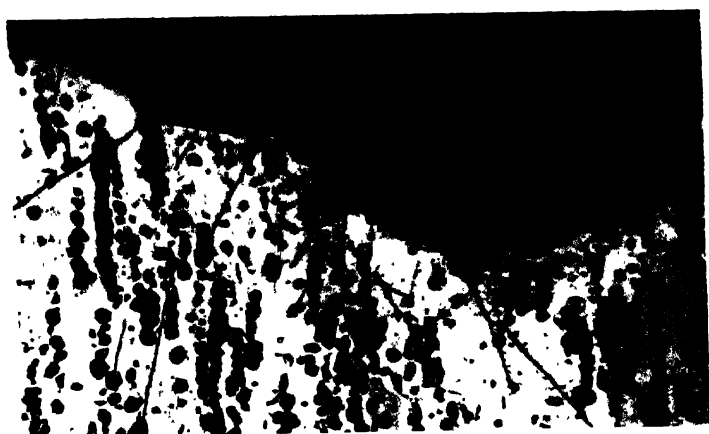
Figs. 75 and 76. Cleavage cracks near fracture of tensile test piece of stainless iron containing 0·08% carbon and 15·4% chromium. × 50.

TABLE XIX.

Mechanical Properties of High Chromium Iron.

(Bars treated : 1⅛″ diameter).

Carbon % .	Silicon . %	Manganese %	Chromium %	Nickel
0·10	0·22	0·23	17·9	0·28

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.		
A.H. 950° C.	20·9	30·8	30·0	44·6	156	3	3	3
„ W.Q. 500° C.	21·6	31·2	32·0	61·5	166	3	3	3
„ „ 600° C.	21·6	29·0	37·0	65·6	156	5	4	5
„ „ 700° C.	18·0	27·8	40·5	66·8	156	3	3	3
„ „ 800° C.	20·0	29·0	37·0	64·8	163	4	4	4

cold working operations, but the latter seems to be an almost inherent feature of the high chromium ferrite which forms by far the greater part of their structure. It appears to be connected with the fact that this constituent possesses strongly defined cleavage planes. Figs. 75 and 76 are of interest in this connection ; they are taken from a broken tensile test piece of iron containing 0·08 per cent. carbon, 0·18 per cent. silicon, 0·05 per cent. manganese, 15·4 per cent. chromium and 0·23 per cent. nickel which had been oil hardened at 1,000°C. and then tempered at 700°C., and represent the structure close to the actual tensile fracture. The cracks in the ferrite grains, so obviously following well marked cleavage planes, suggest very strongly a brittle material.

Probably the chief use of these very high chromium irons will be in the form of sheets, etc., for domestic or ornamental purposes, for which their great softness, when annealed or tempered, and their great resistance to corrosion, make them particularly suitable. . They may be cold worked with ease (for comparison in this respect with the austenitic

chromium-nickel steels, see page 154) and in the form of thin sheets cold pressed to a very considerable extent.

The properties of higher carbon steels, containing more than about 15/16 per cent. chromium depend largely on whether their composition lies in the range of hardenable steels or not.   An example of the former is given in Table XX while Table XXI details the results obtained on a few which belong to the unhardenable variety.   The latter, like the high chromium irons, possess very low impact values and it does not seem to be possible to improve these values by any form of heat treatment.   Steels of the hardenable type, such as that described in Table XX are not used to any great extent.   Owing to their high carbon content, necessary to make them amenable to heat treatment, they are not greatly superior in their corrosion resisting powers to material of lower chromium and carbon contents which may be heat treated to give similar mechanical properties.   This is due to the fact that a large amount of the chromium in such steels exists, after hardening and tempering or annealing, as particles of carbide which are distributed through the ferrite matrix and, in this form, chromium is not useful for promoting resistance to corrosion, see Chapter V.

TABLE XX.

Mechanical Properties of Hardenable Chromium Steel.

(Bars treated : 1⅛″ diameter).

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·53	0·22	0·29	16·8	—

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.
O.H. 900° W.Q. 650° C.	46·0	56·0	19·0	40·6	262	17 15 16
,, ,, 700° C.	41·8	53·8	19·0	41·9	255	22 17 19
,, ,, 750° C.	38·0	51·5	22·5	45·9	223	26 26 24
,, ,, 800° C.	34·4	50·0	26·0	47·2	235	24 23 24

TABLE XXI.

Mechanical Properties of Non-Hardenable High Chromium Steels.

No.	Carbon	Silicon %	Manganese %	Chromium %	Nickel %
1	0·28	0·44	0·44	18·6	0·27
2	0·21	0·86	0·18	20·1	0·26
3	0·26	0·56	0·17	23·6	0·40
4	0·42	0·78	0·82	25·0	0·48
5	0·24	0·63	0·50	28·1	0·26
6	1·03	0·34	0·12	29·9	0·22
7	0·19	0·81	0·38	35·4	0·36

No.	Treatment.	Yield Point, tons per sq. inch.	Maxmium Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduc. tion of Area per cent.	Izod Impact, ft. lbs.		
1	O.H. 950° C. W.Q. 700° C.	17·9	35·0	31·0	57·0	15	12	15
2	O.H. 1000° C. ,, ,,	26·4	37·0	28·0	61·0	5	3	4
3	A.H. 950° C. ,, ,,	—	37·2	28·0	49·7	2	2	2
4	As rolled	37·8	47·2	21·5	39·2	3	3	2
	W.Q. 1000° C.	26·0	42·8	26·5	51·0	1	2	1
5	As rolled	30·5	41·3	22·0	45·9	2	2	3
	Annealed 825° C.	25·6	37·8	30·0	52·2	3	3	3
	,, 930° C.	21·6	37·4	31·0	55·8	2	2	2
6	A.H. 950° C. W.Q. 700° C.	24·0	45·2	7·5	6·7	1	1	1
7	W.Q. 800° C.	32·8	38·8	28·0	45·9	3	3	4

Modulus of Elasticity in Tension (Young's Modulus). The results given in Table XXII and obtained from a series of stainless steels with differing carbon content, show that the value of Young's Modulus of stainless steel is similar to, though possibly somewhat higher than, that of carbon steel, The bars in all cases were oil hardened, sample A from 1,000° C., the others from 950° C., and then fully tempered at 700° to 725° C.

Determinations have also been made at Woolwich Arsenal on a series of steels* which had been oil hardened and tempered at various temperatures. In most cases the steels were hardened both from 950° and 1,000° C. and

* "Metallurgical Data on Stainless Steels." H. H. Abram. *Chem. & Met. Eng.*, Vol. XXX, p. 430 (1924).

TABLE XXII.

Modulus of Elasticity in Tension of 12/14 per cent. Chromium Steels.

	A.	B.	C.	D.	E.
Carbon % ...	0·09	0·12	0·17	0·21	0·23
Chromium % ...	12·0	12·1	14·4	11·5	12·8
Max. Stress (tons per sq. inch) ...	43·5	41·3	44·6	53·4	50·2
Modulus of Elasticity (lbs. per sq. inch) ...	$29·6 \times 10^6$	$30·8 \times 10^6$	$29·8 \times 10^6$	$30·2 \times 10^6$	$30·6 \times 10^6$

TABLE XXIII.

Modulus of Elasticity in Tension of 12/14 per cent. Chromium Steels (Second Series).

Steel.	Carbon. %	Silicon. %	Chromium. %	Range of Tensile Strength, Tons per sq. inch.	Mean Value of Young's Modulus, Lbs. per sq. inch.	
1.	0·10	0·08	12·85	41·3 to 52·5	31·7	10^6
2.	0·15	0·11	13·5	43·6 to 59·8	31·2	10^6
3.	0·17	1·35	13·9	42·4 to 57·6	29·6	10^6
4.	0·31	0·31	14·2	48·7 to 67·7	32·1	10^6
5.	0·35	1·43	14·7	53·7 to 69·7	32·0	10^6
6.	0·48	0·13	12·37	50·4 to 63·9	32·3	10^6

temperatures of 600°, 650° and 700° C. used for tempering. The range of tensile strength obtained from each steel and also the mean value of the modulus, is given in Table XXIII.

These values are in good agreement with those given in Table XXII.

Modulus of Elasticity in Shear.— The figures obtainable from stainless steel are indicated by the results of the following torsion test on material containing :—

Carbon	...	...	0·25 per cent.
Silicon	...	...	0·18 per cent.
Manganese	...	...	0·22 per cent.
Chromium	...	...	12·5 per cent.
Nickel	...	...	0·21 per cent.

The test bar was air hardened from 925° C. and tempered at 675°C. and gave a Brinell hardness number of 255, corresponding to a tensile strength of 55 tons per square inch.

Stress at Limit of Proportionality ...16·0 tons per square inch.
Stress at Yield Point ...   .32·9 „   „   „
Maximum Stress   ...   .47·3 „   „   „   •
Total Twist in 4" (Test piece 0·5" dia.)..1140 degrees.
Modulus of Elasticity in Shear   ...12·5 × 10⁶ lbs. per sq. inch.

Effects of Cold Work.

It is not intended to describe here the conditions under which high chromium irons and steels may be cold-worked in various ways, some consideration will be given to this in a later chapter, but to set out some of the properties of cold worked material and the effects of heat treatment thereon.

Most, if not all, metals harden when cold-worked ; but they do not all harden at the same rate. As this point is of considerable importance in the application of cold-working operations to different metals, particularly in connection with different types of stainless steels, it may be useful to consider briefly a method for comparing the rate at which different metals harden when submitted to cold work. In looking for such a method, it was considered desirable that it should be readily standardised, be easily applied, require only a small amount of material and give indications which would distinguish readily different capacities for work-hardening. The following method appears to fulfil these conditions. Small cylinders of standardised size, that adopted being 0·95 inches long and 0·625 inches diameter, were compressed 10 per cent., 20 per cent., 30 per cent. and occasionally 40 per cent. and 50 per cent. of their length. The load necessary to do this was observed and also the Brinell hardness values of the samples before and after compression. As probably the hardness of a compressed sample would not be completely uniform throughout, the Brinell impression was always obtained on a flat, half-an-inch wide, filed or ground on the side of the sample. Tests carried out in this manner on a number of chromium irons and steels indicate that these work-harden at substantially the same rate, irrespective of their initial hardness, and moreover that this rate is practically the same as that of ordinary mild steel tested under the same conditions. For example, the curves in Fig. 77 show the

increase in Brinell hardness of ordinary mild steel and of various chromium steels and it is evident that the slope of all the curves is substantially the same.
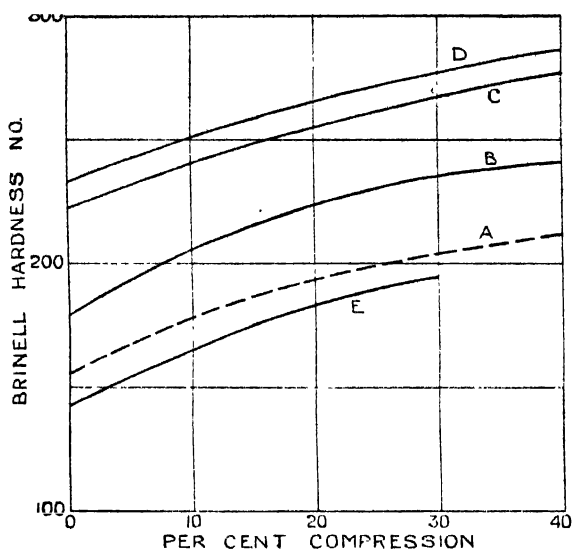
Fig. 77. Work Hardening Tests.

Curve.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Treatment.
A.	0·15	0·26	0·70	—	—	A.H. 900° C.
B.	0·10	0·42	0·19	13·5	0·27	A.H. 950° C., T. 700° C
C.	0·16	0·10	0·08	12·0	0·45	,,
D.	0·26	0·19	0·20	13·2	0·65	,,
E.	0·10	0·31	0·10	20·4	0·30	,,

From a corrosion resisting point of view, it is undesirable to put into service, in a drastically cold-worked condition, an article made of the lower chromium stainless irons and steels. The production of very high tensile wire or strip from these materials by heavy drawing or rolling is therefore not generally to be recommended. This may limit their use for certain purposes, but a considerable range of tensile strength, probably from about forty to eighty or a hundred tons per square inch, may be obtained by judicious combinations of composition, heat treatment and drawing. As giving some indication of the increase in tensile strength

produced in wire by given reductions in diameter, Fig. 78 may be cited. This diagram also indicates that, as in Fig. 77, the rate of work-hardening appears to be independent of the composition of the steel or of its initial hardness.

Further details regarding the tensile tests on wires, which are plotted in Fig. 78, are given in Table XXIV.
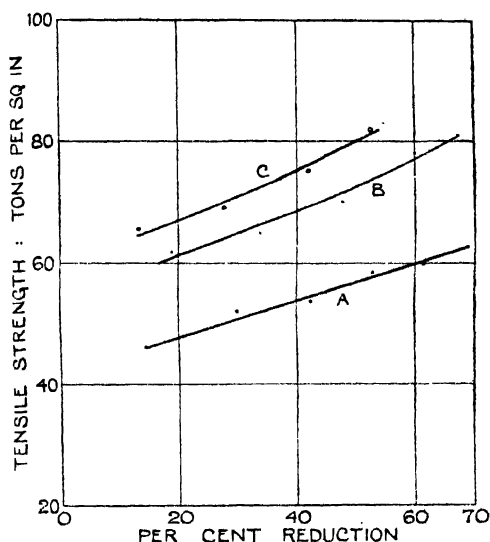
FIG. 78. Tensile strength of stainless steel wire after drawing.

Curve.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Previous Treatment.
A.	0·10	0·10	0·12	10·6	0·26	4G. rod, hot rolled and T. 700° C.
B.	0·10	0·10	0·12	10·6	0·26	10G. wire, A.H. 950° C.
C.	0·30	0·13	0·15	13·4	0·20	4G. rod, A.H. 950° C., T. 600° C.

The effect of reheating work-hardened material to gradually increasing temperatures is indicated in Fig. 79. In this case softening commences between 600°C. and 650°C. and continues with increasing temperature until the material commences to harden again owing to the Ac.1 change. The temperature at which softening commences is, however, affected by the degree of work-hardening to which the material has previously been submitted. The tests given

TABLE XXIV.

Tensile Tests on Stainless Iron and Steel Wires.

Mark.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A B	0·10	0·10	0·12	10·6	0·26
C	0·30	0·13	0·15	13·4	0·20

Mark.	Prior Treatment.	Reduction %	Maximum Stress, tons per sq. inch.	Elongation per cent. (L = 8D.).	Reduction of Area %
A	4G rod, hot rolled and T. 700° C.	15·5	46	10·5	69·8
		30·0	52	11·0	64·8
		42·5	53·6	14·2	63·7
		53	58·5	10·0	59·6
		61·5	59·9	8·7	60·0
B	10G. wire, A.H. 950° C.	19	61·8	8·7	57·5
		34	64·7	8·45	57·8
		48	70·0	8·1	54·6
		60	78·0	7·8	50·4
		67·5	81·0	6·7	49
C	4G. rod, A.H. 950° C., T. 600° C.	18·5	65·5	10·6	42
		28	69	8·75	40
		42	75	8·6	39
		52·5	82	7·7	31

in Table XXV on heavily drawn stainless iron wires, show that these were softened considerably by reheating at 500°C. The reverse bend test, mentioned in this Table, was carried out by holding the sample in a vice, which had the inner edges of the jaws rounded to a radius of 5 mm. The projecting end of the wire was then bent at right angles to the fixed part, first to one side then to the other, until it broke. The number of bends through 180° was noted, the first bend through 90° not being counted.

The material used for this wire was the same as that used for the series of tests given in Table I (page 101) and Fig. 69; it is interesting to note the similarity in tensile strength between the cold-worked samples and those oil

hardened, after both had been tempered at the same temperatures. It would also appear from the results in Table XXV that the tensile strength of the cold drawn wire is reduced to about 60/65 tons per square inch, on tempering at 500°C., no matter what its strength was before tempering, providing, of course, that the strength, as drawn, exceeded the range mentioned.
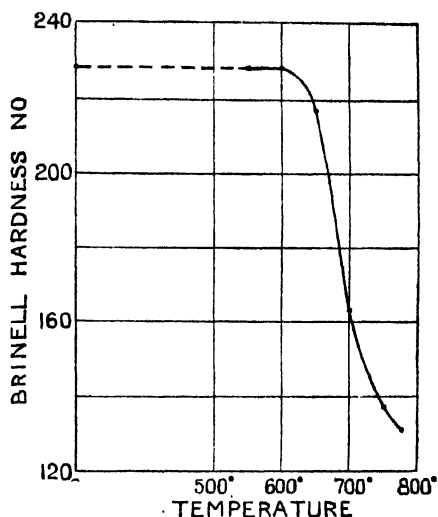
Fig. 79. Effect of re-heating on the hardness of cold-worked Stainless Iron (0·08% carbon, 12·3% chromium). Samples previously compressed 55%.

TABLE XXV.

Tests on Hard Drawn Stainless Iron Wires.

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·07	0·08	0·12	11·7	0·87

Gauge.	Diameter, inches.	As Drawn.		Tempered 500° C.		Tempered 600° C.		Tempered 700° C.	
		Max. Stress, tons per sq. inch.	Reverse Bend Test.	Max. Stress, tons per sq. inch.	Reverse Bend Test.	Max. Stress, tons per sq. inch.	Reverse Bend Test.	Max. Stress, tons per sq. inch.	Reverse Bend Test.
11	·111	68	5	59·5	6	46	8	36	9
14	·0804	78	5	64·5	7½	50	16½	89·5	15
15	·0706	89	5	61	9	49	18	38	18
17	·0568	114	4	67	11½	50·5	20	40·5	27
18	·0465	108	18	61	22	46	30	39	41

The results of a study* of low temperature annealing on cold-drawn stainless iron and steel rods are given in Table XXVI. The material was in the form of rods, ⅜ inch diameter, which were commercially described as " cold drawn, ground and polished." As will be seen, an annealing at 300°/375°C., in the case of the stainless iron, or 375°/450°C., in the case of the stainless steel, results in a very marked improvement of the elastic properties of the cold-drawn rods. In this respect, stainless material behaves in a similar manner to carbon steels.

TABLE XXVI.

Properties of Cold Drawn Stainless Steels after Annealing at Low Temperatures.

	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
Stainless Iron ...	0·12	0·16	0·13	12·0	0·25
,, Steel ...	0·40	0·52	0·24	13·0	0·06

Treatment.	Tensile Test.					Compression Test.	
	Elastic Limit, tons per sq. inch.	Yield Point, tons per sq. inch.	Max. Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Elastic Limit, tons per sq. inch.	Yield Point, tons per sq. inch.
STAINLESS IRON—							
Cold drawn, as received	7	32	37·2	28·5	70	9	28
Ann. 1 hour at 100° C.	8	32	37·2	28	70	9	28
,, ,, 200° C.	14	32·5	37·6	27	70	12	27
,, ,, 300° C.	22	33	38·0	24	69	18	30
,, ,, 375° C.	22	26	34·0	32	73	20	26
,, ,, 450° C.	19	26	34·0	32	72	19	26
,, ,, 650° C.	18	20	32·8	37	74	16	21
STAINLESS STEEL—							
Cold drawn, as received	9	39	50·8	21	50	7	35
Ann. 1 hour at 100° C.	10	39	50·8	21	52	10	34
,, ,, 200° C.	17	40	51·2	19	50	17	36
,, ,, 300° C.	24	43	50·8	20	52	22	37 ⅜
,, ,, 375° C.	29	40	50·4	21	52	26	35·5
,, ,, 450° C.	28	39	50·4	22	53	25	35
,, ,, 550° C.	26	35	49·2	22·5	55	26	33·5
,, ,, 650° C.	24	32	48·4	25	57	23	32·5
,, , ,, 780° C.	24	31	47·6	26	57	25	31·5

* " Effect of Low Temperature Annealing on Some Mechanical Properties 'of Cold Drawn Steels." S. H. Rees. *J.I.S.I.*, 1923, Vol. II, p. 273.

THE INFLUENCE OF OTHER ALLOYS ON THE PROPERTIES OF HIGH CHROMIUM STEELS

CHAPTER IV

THE INFLUENCE OF OTHER ALLOYS ON THE PROPERTIES
OF HIGH CHROMIUM STEELS

Like ordinary carbon steels, the high chromium steels described in the previous chapters, when produced commercially, contain small amounts of other elements whose presence is accidental or more or less unavoidable. As the amounts of these elements are likely to vary to a certain extent, it is important to determine how such variations are likely to affect the structure and mechanical properties of the steels. The most important of such variables in these steels are silicon and nickel. Manganese may also vary to some extent, though generally not in any very great degree. Steels made by aluminothermic processes may also contain small but influential amounts of aluminium. The presence of these various metals is more or less accidental, but the properties of the steel may be appreciably affected thereby.

Besides these accidental differences, however, deliberate additions of the metals mentioned above or of others such as copper, cobalt, molybdenum and tungsten have been suggested, and in a number of cases are regularly used, in order to develop special properties in stainless steels. Several of the complex steels thus produced have valuable properties and their use has developed considerably during the past few years. In this chapter, it is intended to summarise the effects of such additions, whether accidental or otherwise, on the structure and physical properties of high chromium steels.

(a) Chromium-Nickel Steels.

Of all the metals added to high chromium steels in order to improve their properties, nickel is easily the most important. It profoundly affects the physical properties of the steel and has a notable influence on its resistance

to corrosion. The high chromium-nickel steels, in fact, form a very important series of corrosion-resisting materials and they are also the base of still more complex alloys which are being developed to combat particularly severe forms of corrosive attack.

The effect of the addition of nickel to ordinary carbon steels is well known; it lowers the temperatures at which the various structural changes occur in the steel and also retards quite considerably the rate at which they take place on cooling. This is indicated by the widely known effect of nickel on the hardening capacity of steel, an effect very similar to that of chromium already described in these pages. Thus ordinary mild steel requires cooling at a very fast rate if it is to be hardened, so fast indeed that, when in the form of a bar one inch or so in diameter, it is impossible to cool it quickly enough to harden it completely, even by quenching it in cold water. By adding about 8 per cent. nickel to the steel, a bar of similar size will harden readily if quenched in oil. A larger amount of nickel, e.g., 10 or 12 per cent., produces an air-hardenening steel while still more, 25 per cent. or so, makes the steel austenitic. The effect of nickel in thus altering the hardening capacity of steel is well summarised in the diagram due to
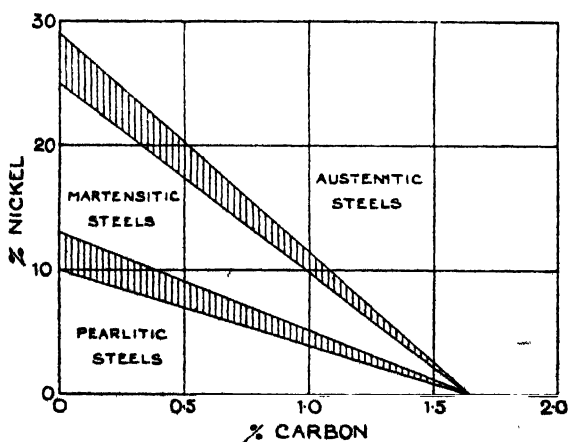
Fig. 80. Influence of nickel on the structural characteristics of steels (Guillet).

Guillet and reproduced in Fig. 80, in which are indicated the amounts of nickel necessary to produce martensitic

(i.e. air hardening) and austenitic steels; the diagram also indicates that these amounts are influenced very considerably by carbon content. As nickel and chromium, when added singly to steel, alter its hardening capacity in much the same way, it is to be expected that the action of one will reinforce that of the other when both are present. The nickel-chromium steel so frequently used for automobile and other engineering work is a familiar example of this : A steel containing 0·35 per cent. carbon and 3·5 per cent. nickel hardens readily when quenched in oil from suitable temperatures but is quite soft when air cooled, in the form of bars one inch or so in diameter, from the same temperatures. If the nickel be replaced by about 1·5 per cent. chromium, the carbon content remaining the same, the material will behave in much the same fashion when similarly heat treated. If, however, the steel contains both 3·5 per cent. nickel and 1·5 per cent. chromium, it will harden when cooled freely in the air from hardening heats, its Brinell hardness value in that condition being practically the same as when oil quenched from the same temperatures. It may be expected therefore that if nickel be added to a high chromium steel, the hardening capacity of the latter will be increased and finally, with sufficient nickel, the steel will become austenitic. According to Strauss and Maurer,[*] the amount of nickel required in a steel of given chromium content to produce completely austenitic material is given by curve B in Fig. 82 (p. 144); the amount is lower, the higher the chromium content, as might have been predicted.

(1) STEELS WITH 12/14 PER CENT. CHROMIUM.

It will be useful in studying the influence of nickel on chromium steels if consideration is first given to the effect of increasing gradually the nickel content of steel containing 12/14 per cent. chromium and about 0·8 per cent. carbon. Most commercial samples of this steel, used so widely for " stainless " cutlery, contain small amounts of nickel, generally less than one per cent. As a rule, this nickel is not purposely added but comes from the raw materials used in steel making; owing to the prevalence in the use of alloy steels for engineering work, much of the

* " Die Hochlegierten Chromnickelstähle als Nichtrostende Stähle." *Kruppsche Monatshefte*, August, 1920, p. 129.

better quality steel scrap on the market contains appreciable
quantities of nickel. The nickel thus present lowers the
temperatures at which the structural changes occur in the
steel, particularly those on cooling ; it increases the hardening
capacity of the steel and also retards to some extent its
tempering after hardening. It may thus alter materially
the mechanical properties of the material. The effects on
the hardening and tempering of the steel may be illustrated
by the curves on Fig. 81. These represent the Brinell
hardness numbers obtained from a series of five stainless
steels in which the nickel content varied from 0·26 to 1·60,
the composition with regard to other elements being sensibly
constant. The samples were first oil hardened from 900° C.
and then tempered at gradually increasing temperatures.
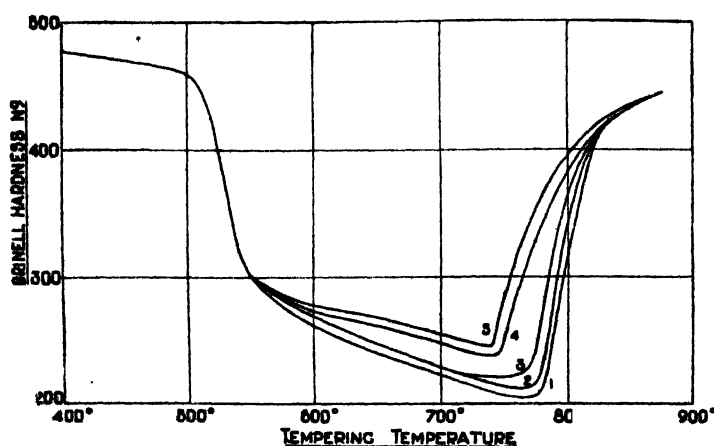
Fig. 81.   Effect of nickel on the hardening and temper
steel :

No.	Carbon, %	Chronium, %	Nickel, %
1	0·34	11·3	0·26
2	0·38	11·0	0·60
3	0·33	11·0	0·98
4	0·41	11·2	1·25
5	0·38	11·1	1·60

They were quenched out in water from each tempering heat
and their Brinell values determined. The results indicate that
nickel has no appreciable effect on the hardness of the steel
after hardening at 900° C. or when subsequently tempered up
to 550° C. Above that tempering temperature, however, the

nickel retards the tempering considerably, causing the high nickel steels to be distinctly harder after tempering at a given temperature than those with lower nickel content.   In addition, owing to the effect of nickel in lowering the temperature at which the Ac.1 change occurs, the tempering range of the high nickel steels is considerably shortened ; this, by precluding the use of the highest tempering temperatures possible with a steel of low nickel content, also increases the difference between the maximum softness obtainable on tempering steels of low and high nickel content.   The effect is probably exhibited in the most striking manner by comparing the results obtained from steels Nos. 2 and 5 in Fig. 81.   These two steels, except for their nickel content, are almost identical in analysis.   The former with 0·6 per cent. nickel, after tempering at 750° to 775° C., gave a Brinell hardness number of 215, equivalent to a tensile strength of 46 to 47 tons per square inch.   On the other hand, steel No. 5, with 1·6 per cent. nickel, reached its maximum softness at 720°/740° C., giving a Brinell hardness number of 244, equivalent to a tensile strength of 58 tons per square inch.   Tempering the two steels at 700° C. gave hardness numbers of 228 and 255 respectively, these being equivalent to tensile strengths of 50 and 55 tons per square inch.

The influence of nickel in intensifying the air hardening capacity of the steel may perhaps be illustrated by figures obtained from experiments carried out with the object of finding the necessary conditions for annealing the high nickel steels, in other words, determining the fastest rate of cooling which will prevent the steel from hardening. Samples of steels Nos. 1 and 5 (Fig. 81) were heated to 900° C. and, after soaking for half-an-hour, were transferred to furnaces at 700°, 650° or 600° C. (being air cooled approximately to the temperature of the second furnace before placing therein) and held at these temperatures for varying periods after which they were quenched out in water and their Brinell hardness numbers determined.   A similar series was also carried out using an initial temperature of 1,060° C. The results obtained are given in Table XXVII.   This method of treatment, consisting of holding the steel, during its cooling from a hardening heat, at a temperature somewhat below that at which the Ar.1 change normally occurs, is

a very effective way of annealing ordinary stainless steels; it is described on page 474. Obviously, the longer the steel has to be held at such a temperature in order that the change from austenite to pearlite may take place completely, the slower the rate it may be cooled from a hardening heat and yet be hardened.

TABLE XXVII.

Initial Temperature.	Steel No.	Nickel %	Time in Second Furnace	Temperature of Second Furnace.		
				700° C.	650° C.	600° C.
900° C.	1	0·26	½ hour.	188	228	228
			1 hour.	179	228	228
			2 hours.	179	228	228
900° C.	5	1·60	½ hour.	444	340	340
			1 hour.	387	255	269
			2 hours.	382	228	228
1,060° C.	1	0·26	1 hour.	196	217	217
			2 hours.	192	217	217
			4 hours.	192	212	217
			8 hours.	188	202	217
1,060° C.	5	1·60	1 hour.	578	321	269
			2 hours.	495	277	255
			4 hours.	460	241	217
			8 hours.	351	228	217

These results show that whereas the low nickel steel was easily annealed in each experiment, the high nickel steel required a more prolonged soaking in order to anneal it. The results also show that the Ar.1 point in the high nickel steel probably occurs at a somewhat lower temperature than 700° C. even on very slow cooling.

With increasing content of nickel, the change austenite to pearlite occurs with still greater difficulty, such steels requiring a very slow rate of cooling in order to anneal them. Thus samples of steel containing 0·39 per cent. carbon, 10·5 per cent. chromium and 2·24 per cent. nickel, were re-heated to 900° C. and 1,060° C., respectively, transferred to a second furnace maintained at 600° to 650° C. and after being held there for different periods, were quenched out in

water. They then gave the following Brinell hardness numbers :—

Held at 600°/650° C.		Initial Temperature.	
		900° C.	1,000° C.
For 1 hour and W.Q.		477	555
For 2 hours ,, ,, ...		402	477
For 4 ,, ,, ,, ...		290	340
For 8 ,, ,, ,, ...		—	290
For 24 ,, ,, ,, ...		248	269
For 72 ,, ,, ,, ...		241	241

The samples held at 600°/650° C. for 72 hours still contained a small amount of martensite after quenching.

The dominant action of these small amounts of nickel being thus to increase the ease with which the steel may be hardened, their particular effect on the mechanical properties of a given chromium steel will depend on whether the latter hardens intensively or not. If the plain chromium steel

TABLE XXVIII.

Influence of Nickel on the Mechanical Properties of Stainless Steel.

Steel.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A.	0·39	0·08	0·10	10·0	0·42
B.	0·39	0·12	0·32	10·5	2·24

Steel	Treatment.	Yield Point, tons per sq. inch	Maximum Stress, tons per sq. inch	Elongation % on 2 ins.	Reduction of Area %	Brinell Hardness No.	Izod Impact, ft. lbs.
A.	O.H. 900° W.Q. 600° C.	49·0	64·2	15·0	45·9	302	22 19 20
	,, ,, 650° C.	39·6	55·8	18·5	54·6	262	25 28 26
	,, ,, 700° C.	31·2	49·6	24·5	58·6	235	75 66 72
B.	O.H. 900° W.Q. 600° C.	53·2	62·7	17·0	48·5	293	16 18 —
	,, ,, 650° C.	46·4	59·0	20·0	52·2	277	30 29 26
	,, ,, 700° C.	45·2	58·4	21·0	51·0	269	32 34 33

hardens well, the effect of small nickel additions will be noticeable mainly in tempering operations, as already indicated in Fig. 81. In such cases the nickel does not appear to affect appreciably the toughness or ductility of the steel. Thus the results given in Table XXVIII, obtained from bars 1¼ inches in diameter, indicate that the higher nickel steel has properties similar to those of the one containing a less amount when the two are tempered to give the same tensile strength.

If, however, the composition of the straight chromium steel is such that its air hardening capacity is not great, the addition of small amounts of nickel may affect very considerably its mechanical properties after given heat treatments. For example, stainless irons containing about 14 per cent. of chromium do not air harden to any

TABLE XXIX.

Influence of Nickel on the Mechanical Properties of Stainless Iron and Mild Stainless Steel.

Treatment : A.H. 950°C., W.Q. 700°C.

Carbon %	Chromium %	Nickel %	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell		Izod Impact, ft. lbs.
							Hard'd.	Temp'd.	
0·09	13·7	0·10	29·6	37·1	32·5	68·8	241	179	100, 96, 106
0·08	13·3	0·46	34·4	40·7	32·0	68·8	340	217	98, 98. 101
0·08	13·6	0·80	39·0	45·0	29·0	63·7	351	241	86, 86, 88
0·10	14·1	1·23	40·0	48·6	25·5	55·8	418	255	65, 62, 65
0·21	13·3	0·80	30·0	44·0	26·0	61·5	286	207	40, 36, 38
0·22	12·8	0·74	38·0	48·4	25·5	60·4	387	228	60, 55, 60
0·22	13·3	1·22	45·4	52·4	24·5	59·3	477	248	51, 48, 48

great extent when in the form of bars one inch or so in diameter, as has already been indicated. The addition of about 1 per cent. of nickel, however, increases their air-hardening capacity so markedly that the properties of the material, after air hardening and tempering, depend considerably on its nickel content. This may be illustrated by the results given in Table XXIX. All the steels were heat-treated in the form of bars 1¼ inches diameter.

Obviously the size of the piece treated will influence considerably the effect which the added nickel may have. Very small bars will cool sufficiently quickly, when air-cooled, to allow low nickel material to harden quite well, while the much slower rate of cooling obtained with bars considerably larger than one inch in diameter, will reduce the hardness of the higher nickel irons or steels ; both these effects would tend to reduce the difference in mechanical properties caused by varying nickel content.

Whether the presence of these small amounts of nickel is advantageous or not will depend on the purpose for which the steel is used. If bars or forgings of large size have to be hardened and tempered, a content of 1 per cent. nickel or thereabouts may be a decided help during heat treatment operations ; it will enable the steel to air-harden more effectively, especially if the chromium content is in the neighbourhood of 14 per cent. If, however, the production of small articles is in question—particularly of stainless steels rather than irons—the presence of a similar amount of nickel may be the reverse of advantageous ; it is likely to increase the danger of cracking during cooling after rolling or forging operations and it makes annealing treatments more prolonged, should these be necessary. In the case of stainless irons, where the hardening effect is so noticeable, the presence of considerable amounts of nickel is undesirable when soft material is required ; for such purposes the nickel content of irons, containing up to about 14 per cent. chromium, should not exceed 1 per cent. ; it is so limited, for example, in a number of aircraft specifications.

The chromium-nickel series of stainless steels form the subject of the well-known Krupp patents* which comprise steels containing 7 to 40 per cent. chromium, 0·5 to 20 per cent. nickel and not more than 1·0 per cent. carbon. This range of composition includes both martensitic and austenitic steels and, of the former type, Messrs. F. Krupp, A.G., have manufactured several varieties which are similar in analysis to those described in the last few paragraphs. Their first steel of this type, " V. 1. M.", contained 12/14 per cent. chromium and 1·5/2·0 per cent. nickel together with

* German patents 304,126 (Oct., 1912) and 304,159 (Dec., 1912). British patents 13,414 and 13,415 (June, 1913).

about 0·2 per cent. carbon, the nickel being an essential constituent.   More recently, however, they appear to have concluded that so much nickel is not always advantageous and have put on the market further steels, "V. 8. M." and "V.5.M.," containing less, typical compositions of these materiâls being :

		Carbon %	Chromium %	Nickel %
"V.8.M." ...	...	0·8/0·45	12/14	0·5/0·7
"V.5.M." ...	...	0·1/0·15	12/14	0·5/0·7

Such an amount of nickel is often accidentally present in stainless steels made according to the Brearley patents. It can hardly be looked upon as an essential constituent of the steel ; it certainly is not from the point of view of resistance to corrosion.

The high nickel steel mentioned on page 142 (as well as the corresponding steel with low nickel content) gave a Brinell
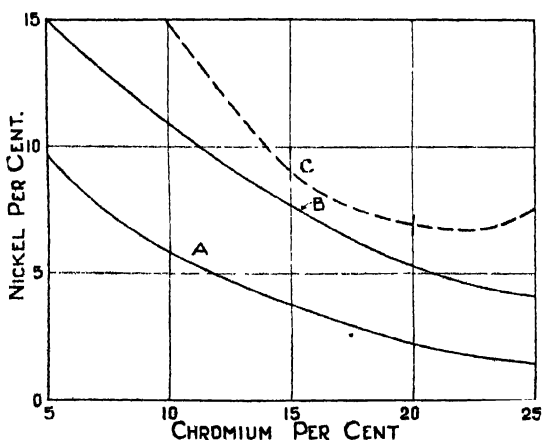
Fig. 82.   Effect of nickel content on the production of austenite in high chromium steels.

Curves A and B—Strauss and Maurer.

Curve C—Bain and Griffiths, see page 158.

hardness number of 555/600 when water quenched in the form of a thin disc from 1,200° C.; that is, it remained completely martensitic.   If the steel contains a somewhat

larger amount of nickel, however, austenite is retained on quenching from such high temperatures, though martensite is still formed on quenching from lower temperatures than these. With still larger amounts of nickel, the temperature leading to the production of austenite is lowered, while the hardness produced on quenching from the temperature range giving martensite, diminishes. Finally, with sufficient nickel, the steel becomes entirely austenitic. The amount of nickel required to produce the several stages in the production of austenite varies with the amount of chromium present in the steel. According to Strauss and Maurer,[*] the amount required in steels containing 0·1/0·5 per cent. carbon is shown in Fig. 82, in which curve A
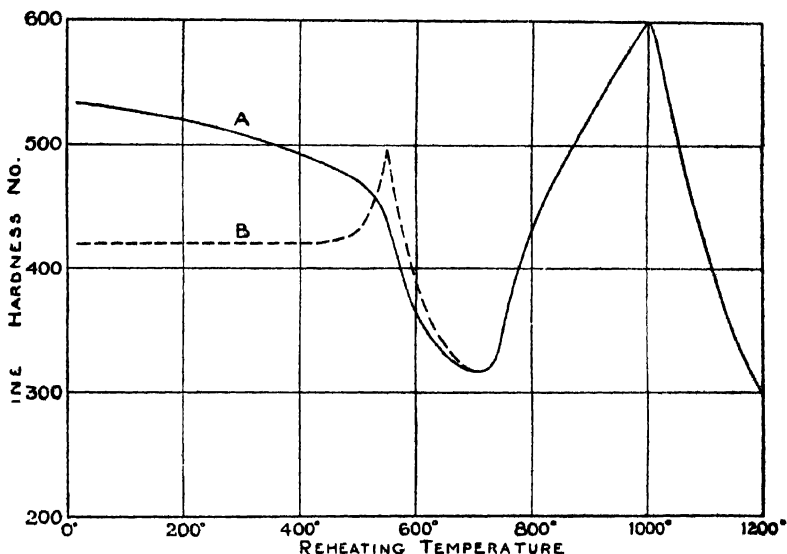
FIG. 83. Relation between Brinell hardness number and reheating temperature of steel containing 0·45 % carbon, 13·1 % chromium, 2·54 % nickel :—

    Curve A. Samples previously W.H. 950°C.
    Curve B.   „   „   W.H. 1,100°C.

indicates the nickel content necessary to give austenite on quenching from high temperatures while a completely austenitic steel is obtained when the nickel content reaches that indicated by curve B. The author has found, however, that austenite is produced, on quenching from high

[*] "Die Hochlegierten Chromnickelstahle als Nichtrostende Stähle," Kruppsche Monatshefte, Aug., 1920.

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temperatures, in steels containing distinctly less nickel than is indicated by curve A in Fig. 82, if the carbon content approaches 0·5 per cent.

The gradual change in properties as the nickel content is raised is well shown by plotting the Brinell hardness numbers obtained on quenching small samples of the steels from successively higher temperatures. Results obtained in this manner from steels containing, respectively, 2·54 and 4·96 per cent. nickel are plotted in Figs. 83 and 84. The full lines, representing the results obtained on reheating samples which had previously been hardened by quenching from 950°C., indicate that the steels in this condition behave in a similar manner to those with lower nickel content. According to Strauss and Maurer's data (Fig. 82), steel A should not become austenitic while steel B is just on the limiting com-
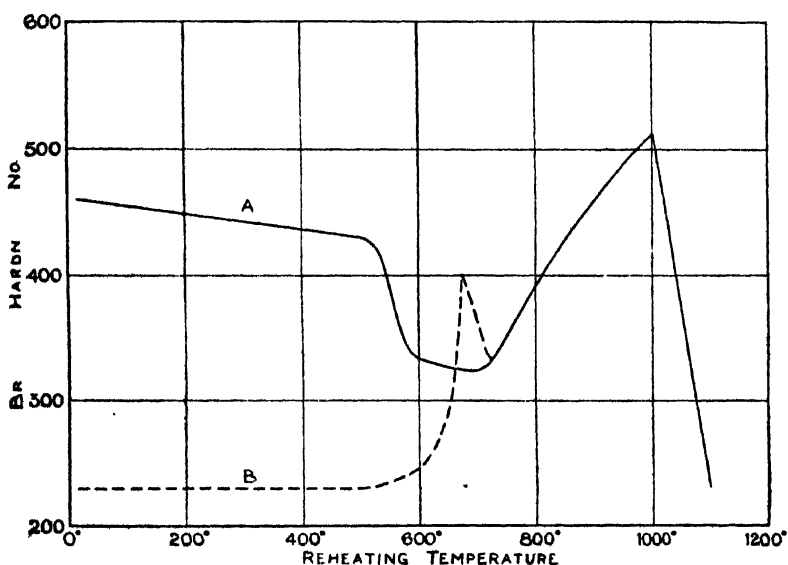
FIG. 84.   Relation between Brinell hardness number and reheating temperature of steel containing 0·28 % carbon, 14·2 % chromium, and 4·96 % nickel.

Curve A.   Samples previously W.H. 950°C.
Curve B.   „   „   W.H. 1,100°C.

position. Austenite was produced, however, on quenching both steels from high temperatures and the dotted lines in Figs. 83 and 84 show that on tempering these austenitic samples, they hardened in the same way as the austenitic·

chromium steels, previously described. The diagrams also show that as the nickel content increases, the austenite becomes more stable, requiring a higher temperature to break it down. This is further illustrated by curve A in Fig. 85, in which are plotted the results of a similar experiment on samples of a steel containing

Carbon ...	0·16 per cent.	
Chromium	13·7 per cent.	
Nickel ...	8·85 per cent.	

which had previously been made austenitic by quenching from 1,100· C. In this case the austenite does not break down until a temperature of about 750°C. is reached and there is no " tempering " range of the martensite so produced as in the steels illustrated in Figs. 83 and 74. Moreover, the hardness produced after reheating this steel in the range 850° to 900° C., and cooling therefrom, increases to some extent with the time of heating in this range. If such
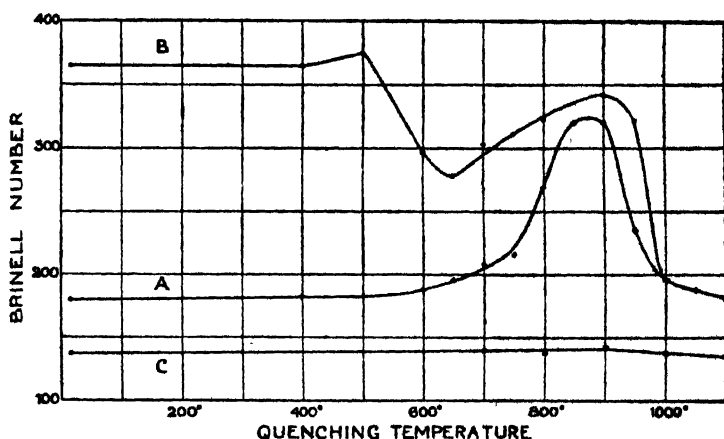
FIG. 85.   Relation between Brinell hardness number and reheating temperature of chromium-nickel steels :—

Curve.	Carbon, %	Chromium, %	Nickel %	Previous Treatment.
A.	0·16	13·7	7·85	W.H. 1,100°C.
B.	0·16	13·7	7·85	Soaked 850/900°C.
C.	0·10	15·2	11·4	W.H. 1,000°C.

hardened material is subsequently tempered, results similar to those shown in curve B, Fig. 85, are obtained. In this case the samples were first given a prolonged heating in the range 850° to 900° C., and when cooled had a Brinell hardness

number of 864. On subsequently reheating, they showed a tempering effect analogous to that of martensitic steels containing a smaller amount of nickel, as indicated in curve B. It is also interesting to note that the maximum tempering effect was obtained in the neighbourhood of 650°C., and that the tempered steel began to harden again at a lower temperature than the austenitic form and also reached a greater hardness.

Steels containing a still greater amount of nickel appear to remain austenitic after reheating to any temperature. Thus curve C, in Fig. 85, shows the Brinell hardness numbers obtained from a steel containing 11·4 per cent. nickel after quenching from the temperatures indicated. These austenitic steels, which have some very valuable properties, will be considered later.

(2) STEELS WITH 17/20 PER CENT. CHROMIUM.

A similar series of changes are produced by the addition of nickel to steels with a higher chromium content. For example, Figs. 86 and 87 give the Brinell hardness values of a series of steels, containing 0·2 per cent. carbon, 20 per cent. chromium and different amounts of nickel, after quenching in water from various temperatures. Whereas the pure chromium steel did not harden appreciably when quenched from any temperature, the addition of about two per cent. nickel produced a steel which not only hardened to a notable extent but also possessed a good impact value when hardened and tempered —see Table XXX, p. 150. Raising the nickel to 4·4 per cent., hardened the steel considerably ; when fully tempered it had a tensile strength of about sixty-five tons per sq. inch. It also became austenitic on quenching from 1050/1100° C. The steels containing 6·6 and 8·4 per cent. nickel were austenitic after quenching from any temperature ; the one with the higher nickel content was, however, distinctly the softer.

The addition of 2 or 3 per cent. nickel to such high chromium steels as these produces a very useful material. As will be seen later, a chromium content of about 17 or 20 per cent. is very valuable when extreme resistance to general corrosion is required ; but the mechanical properties of low carbon steels containing this amount of chromium are not encouraging for many purposes ; they

cannot be hardened appreciably and they have very low impact values, as has been already shown. The addition
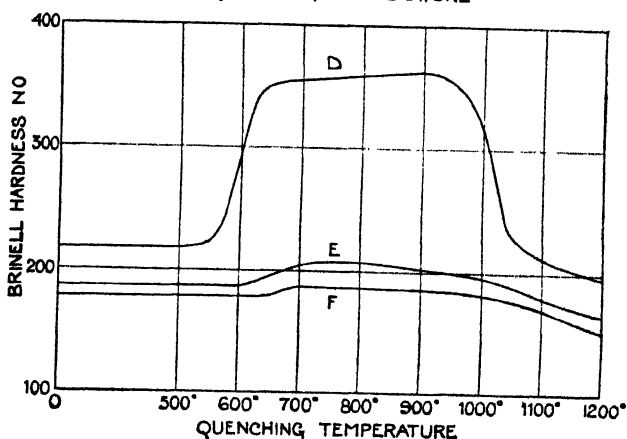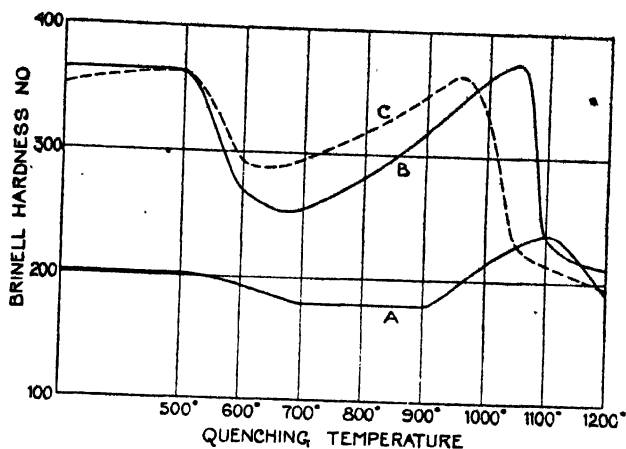
FIGS. 86 and 87. Effect of nickel on the hardening of 20% chromium steels.

Mark.	Carbon %	Chromium %	Nickel %	Previous Treatment.
A.	0·23	19·9	0·27	As rolled.
B.	0·23	19·2	2·16	O.H. 1,000° C.
C.	0·21	19·8	4·40	O.H. 900° C.
D.	0·21	19·8	4·40	W.H. 1,100° C.
E.	0·23	20·5	6·64	W.H. 1,100° C.
F.	0·24	20·2	8·40	W.H. 1,100° C.

of the nickel converts them into hardenable steels which, moreover, possess good impact values. True, it is possible to obtain a hardenable steel containing this amount of

TABLE XXX.

*Effect of Nickel on the Mechanical Properties of 20 per cent.
Chromium Steels.*

Mark.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A.	0·23	0·36	0·18	19·9	0·27
B.	0·23	0·36	0·21	19·2	2·16
C.	0·21	0·34	0·18	19·8	4·40
D.	0·23	0·31	0·34	20·5	6·64
E.	0·24	0·26	0·29	20·2	8·40

(Bars treated : 1″ diameter.)

Mark.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness No.	Izod Impact, ft.		lbs.
A.	O.H.1,000°, W.Q.700°C	26·4	37·0	28·0	61·0	179	5	3	4
B.	„	46·0	55·0	23·0	53·4	255	47	50	46
C.	O.H. 900°, W.Q.600°C	48·0	66·0	17·0	40·6	302	48	40	42
	W.Q.1,100°C.	26·0	69·0 *	30·0	28·0	217	86	74	89
	W.Q.1,200°C.	25·0	64·0	27·5	21·5	196	66	59	56
D.	W.Q.1,050°C.	25·5	67·0	48·0	39·7	196	107	120	120
	W.Q.1,150°C.	18·0	51·7	67·0	60·4	170	110	110	110
E.	W.Q.1,050°C.	27·0	53·0	59·0	51·4	185	115	110	120
	W.Q.1,150°C.	19·2	47·0	67·0	68·8	166	97	107	108

* Both these test pieces broke prematurely.

chromium without the use of nickel, provided one raises
the carbon content to about 0·6 per cent. or more. But,
by so doing, the advantages from a corrosion resistance
point of view of the higher chromium content are largely
nullified, because a considerable amount of the chromium
is then present in the particles of carbide which are distributed
in large numbers through the steel when it is tempered ;
and this part of the chromium is of no value in promoting
resistance to corrosion.

Steels of the 17/20 per cent. chromium, 2 per cent.
nickel type were put on the market some six or seven years
ago by Messrs. Brown, Bayley's Steel Works, Ltd., under
the brand " Twoscore "—the derivation of the name will be
obvious—and have been extensively used in engineering
work. As in the case of the hardenable steels containing

12/14 per cent. chromium, the mechanical properties of "Twoscore" steels vary according to their carbon content and the heat treatment they have received, as will be evident from the figures given in Table XXXI. Due to their nickel content, they commence to harden when air cooled or quenched from temperatures above about 700° C.—see curve B, Fig. 86—but apart from this they respond to tempering in a similar manner to the 12/14 per cent. chromium steels.

TABLE XXXI.

Mechanical Properties of "Twoscore" Steels.
(Bars treated : 1⅛″ diameter).

(A) EFFECT OF VARYING TREATMENT.

Carbon 0·09 per cent. ; Chromium 17·8 per cent. ; Nickel 2·08 per cent.

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.
A.H. 950°C., W.Q. 300°C.	49·6	58·8	20·0	55·8	269	63 89 70
,, W.Q. 400°C.	49·6	58·8	20·0	57·0	269	79 60 61
,, W.Q. 500°C.	46·0	57·8	22·0	59·3	265	96 88 88
,, W.Q. 600°C.	34·4	43·2	28·5	62·2	225	86 75 94
,, W.Q. 650°C.	32·4	42·5	30·0	62·2	217	84 86 88
,, W.Q. 700°C.	?	44·6	28·0	62·2	231	83 83 80
,, W.Q. 750°C.	?	46·5	27·5	59·3	241	81 79 77

(B) EFFECT OF VARYING CARBON CONTENT.

Treatment : A.H. 950°C., W.Q. 650°C.

Carbon %	Chromium %	Nickel %	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. Inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.
0·11	18·0	2·18	36·0	45·3	27·5	62·2	241	87 83 88
0·16	17·2	2·30	38·8	49·0	24·0	61·5	248	68 78 68
0·21	17·6	2·46	39·4	54·8	21·0	53·4	269	50 60 56
0·27	17·9	2·20	45·5	59·5	20·0	55·8	277	46 42 47
0·35	17·4	2·01	57·0	67·3	17·0	47·2	302	20 20 18

With regard to annealing operations, these steels behave in a similar fashion to that containing 10·5 per cent. chromium and 2·24 per cent. nickel described on page 140 ; they may

only be annealed, during cooling from hardening heats, by
very prolonged soaking in the range 600°/650° C.

The value of Young's Modulus for "Twoscore" steels is
similar to that of other hardenable steels; thus tests on twelve
samples of low-carbon material (about 0·1 per cent. carbon)
whose tensile strength varied from forty-five to seventy

TABLE XXXII.

Mechanical Properties of " Twoscore " Steel Sheets.

(A) EFFECT OF VARYING TREATMENT.   (14G. sheet.)

Carbon 0·09 per cent. ; Chromium 18·2 per cent. ;
Nickel 2·2 per cent.

Treatment.	Proof Stress.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 4 ins.	Bend Test.
A.H. 950°C., T.350°C.	52·3	66·8	8·0	180° over 1.T.
,, T.450°C.	55·7	69·9	9·0	,,
,, T.550°C.	54·0	64·4	10·5	180° over ½.T.
,, T.650°C.	39·0	50·7	14·0	180° closed.

(B) TESTS ON SHEETS OF DIFFERENT THICKNESSES.

Carbon 0·09 per cent. ; Chromium 18·6 per cent. ;
Nickel 2·23 per cent.

Treatment : A.H. 950°, T.500°C.

Thickness.	Proof Stress.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 4 ins.	Bend Test.*
8 G.	46·6	57·2	8·0	180° over 5.T.
10 G.	48·9	61·7	10·0	,,
12 G.	53·5	62·1	10·0	,,
14 G.	51·4	59·7	10·0	,,
16 G.	54·1	64·9	9·0	180° over 2.T.
18 G.	49·1	62·4	9·0	,,
20 G.	53·5	58·6	6·5	,,
22 G.	54·5	59·1	9·0	,,
24 G.	51·8	62·8	6·5	,,
26 G.	50·8	60·2	9·0	,,

* The specification to which these sheets were supplied called for a bend test
over 2T for sheets 16G and thinner, and over 5T for sheets thicker than 16G.
The tests were therefore not carried further to determine the limiting radii as in
the tests in part (A).

tons per square inch, gave results between $28\cdot4 \times 10^6$ and $32\cdot1 \times 10^6$ lbs. per square inch with a mean value of $30\cdot1 \times 10^6$. Similarly five steels containing about $0\cdot2$ per cent. carbon and having tensile strengths between fifty-six and seventy-five tons per square inch, had values for the modulus of $28\cdot5 \times 10^6$ to $31\cdot9 \times 10^6$ lbs. per square inch, mean $30\cdot5 \times 10^6$.*

Owing to their very great resistance to corrosion, steels of the " Twoscore " type have been extensively used in the construction of seaplanes and flying boats.   When possessing a carbon content of about $0\cdot2$ per cent., they may be heat treated, in the form of bars or forgings, to give a minimum tensile strength of fifty-five tons per square inch,* together with adequate toughness and ductility (see Table XXXI). The lower carbon material, in the form of sheet, is particularly suitable for the manufacture of various fittings ; these are bent to shape, or are otherwise formed, from the fully softened sheet and are afterwards hardened and tempered to give high values of proof load and tensile strength.   Table XXXII illustrates the effects of varying heat treatment on a sheet of this material and also the results obtained, with constant treatment, on sheets of different thicknesses.

The microstructure of these hardenable chromium-nickel steels is similar to that of the lower chromium steels which harden to the same degree.   When air cooled or quenched from temperatures above the Ac. 1 point, they consist of martensite with or without ferrite or carbide, depending on their carbon content and the quenching temperature ;   on tempering, the martensite changes to sorbite.

Reviewing the data given in the last few pages, it may be said that, broadly speaking, the addition of nickel to high chromium steels results in the production of three types of material :—

(1) Steels, with a small amount of nickel, whose hardening capacity is thereby increased, often advantageously, but which are in the main similar to the hardenable chromium steels.   To this group belong the ordinary stainless steels, in which small amounts of nickel are accidentally present, the Krupp " V.M." steels, and the " Twoscore " steels made by Brown, Bayley's Steel Works, Ltd.

* B.E.S.A. Specification S.80.

(2) Steels containing large amounts of nickel, sufficient to make them completely austenitic. These constitute an exceedingly important group of steels whose properties will be considered presently.

(8) An intermediate group of steels which are either martensitic or austenitic depending on heat treatment. These steels appear to have a very limited use. If made martensitic and then fully tempered, they still remain comparatively hard ; on the other hand, when put in the austenitic condition (for which they require quenching from a very high temperature) they work harden at an extremely rapid rate, so that they can only be machined or otherwise manipulated with great difficulty, if at all.
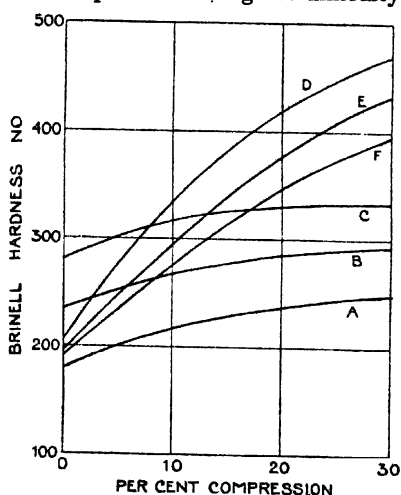
FIG. 88.   Work Hardening Tests ; relation between hardness and degree of compression.

Curve.	Carbon %	Chromium %	Nickel %	Treatment.	Condition.
A.	0·23	19·9	0·27	A.H. 950° C., T. 700° C.	Sorbitic.
B.	0·23	19·2	2·16	,,	
C.	0·21	19·8	4·40	,,	
D.	0·21	19·8	4·40	W.Q. 1,100° C.	
E.	0·23	20·5	6·64	W.Q. 1,000° C.	Austenitic.
F.	0·24	20·2	8·4	W.Q. 1,000° C.	

As the question of work hardening is extremely important, particularly in connection with austenitic steels, it may be useful to consider here the differences between these various

types of steels in relation to the rate at which they harden when submitted to cold work. The effect produced on the rate of work hardening of 20 per cent. chromium steel by the addition of nickel is indicated by Figs. 88 and 89, measurements being made by the method described on page 127. The former diagram connects hardness and amount of compression while the latter gives the loads necessary to produce stated amounts of compression. It should be noted that the steel containing 4·4 per cent. nickel was tested in both the austenitic and the hardened and tempered conditions.
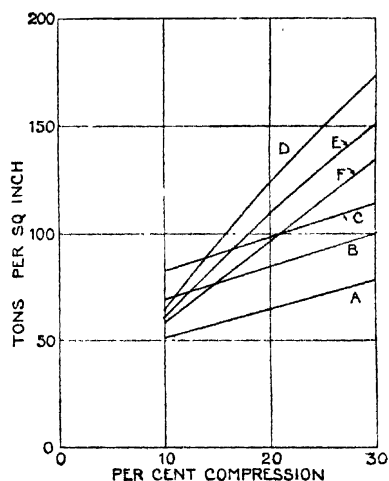
Fig. 89. Work Hardening Tests; loads necessary to produce stated amounts of compression. (See Fig. 88.)

These diagrams possess several notable features. Thus the steels which have been hardened and tempered, work harden at sensibly the same rate, irrespective of their initial hardness, being thus similar to the plain chromium steels already described. On the other hand, the rates of work hardening of the austenitic steels vary considerably among themselves, being greater the lower the nickel content, i.e., the less stably austenitic the steel. But even the one with the highest nickel content work hardens at a much

faster rate than the sorbitic steels, i.e., those which have been hardened and tempered. As a result of this, although a small amount of deformation, 10 per cent. or less in the method of test adopted, is more easily performed on the austenitic steels owing to their low yield point, a considerable degree of compression requires a much heavier
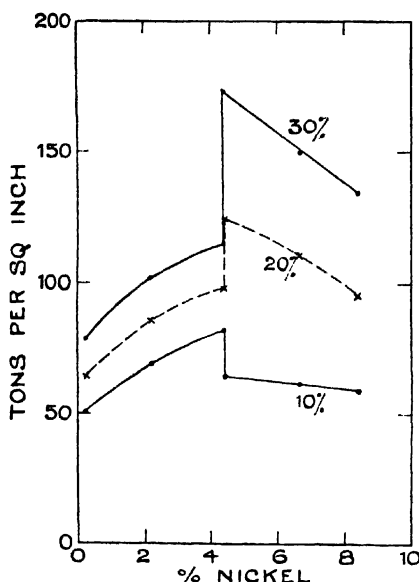
Fig. 90. Effect of nickel content (of 20% chromium steel) on the loads necessary to produce stated amounts of compression.

load in the case of these steels than in that of a sorbitic steel of even greater initial hardness. This effect is strikingly shown in Fig. 90, where the loads required to produce 10 per cent., 20 per cent., and 30 per cent. deformation are plotted against the nickel content of the steel : it should be noted that two values are here plotted for the steel containing 4·4 per cent. nickel ; in each case, at this ordinate, the curve runs to the value for the hardened and tempered form and leaves by that of the austenitic form. One may note that whereas an increase in nickel content necessitates a greater

load to produce a given amount of deformation when the steel is of the hardenable type, due undoubtedly to the increase in initial hardness brought about by the added nickel, it reduces the required load when the steels are austenitic.

(3) PROPERTIES OF AUSTENITIC STEELS.

The austenitic steels produced when sufficient nickel is added to high chromium steels have mechanical properties entirely different from those of the hardenable type previously considered and, owing to their usefulness, they merit a detailed consideration. Apart from those steels in which small amounts of nickel are accidentally present (the ordinary " stainless steels "), these alloys form probably the most useful part of the range of composition covered by the patents taken out by Messrs. F. Krupp, A.G., as a result of the investigations of Drs. Strauss and Maurer (see p. 20) to whom the credit for their discovery is due. The first austenitic steel of this type available commercially was the well-known " V.2.A." made by Messrs. F. Krupp, which contained about 20 per cent. chromium, 7 per cent. nickel, and 0·2 per cent. carbon. About the end of 1923, the British rights for the manufacture of the Krupp steels were secured by the Firth-Brearley Stainless Steel Syndicate and, under their licence, the steels were produced in this country by Messrs. Brown, Bayley's Steel Works, Ltd. (brand " Anka ") and by Messrs. T. Firth and Sons, Ltd. (brand "Staybrite"); they have since been produced, under various trade names, in other countries ; e.g., Allegheny Metal (Allegheny Steel Co., U.S.A.), K.A.2. (Republic Steel Corporation, U.S.A.), and others.

As a result of his investigations on these austenitic steels, investigations carried out over a period of years and to a large extent independently of the work of Strauss and Maurer, the author considered that an alloy containing 15/16 per cent. chromium and 10/11 per cent. nickel possessed the best all-round combination of properties desirable in such a steel for most of the purposes for which it might be used, and hence this is the standard type of the alloy made, under the name " Anka," by the firm with which he is associated. Messrs. T. Firth & Sons, Ltd., largely as a result of Dr. Hatfield's investigations, adopted the composition

18 per cent. chromium and 8 per cent. nickel for the standard form of their material " Staybrite." There is actually little difference between the corrosion resisting properties of " Anka," " Staybrite," and " V.2.A." and, for most purposes, the values found for one of these steels may be applied to the other two ; there are, however, more noticeable differences in their mechanical properties.

From Figs. 85 and 87, one can see that a steel which contains rather less nickel than is required to make it fully austenitic, is hardened appreciably by cooling from the range 700°/1000° C. ; with a higher nickel content, the hump on the Brinell hardness curve (such as that in curve A, Fig. 85) is flattened out and finally by a further nickel addition one obtains a steel which does not harden when cooled from any temperature. According to Strauss and Maurer, curve B in Fig. 82 represents the nickel content required to produce this latter effect with chromium steels of different compositions. More recent investigations by Bain and Griffiths,* who employed drastic methods of annealing in order to break down unstable austenitic structures, gave the higher values indicated by curve C. in Fig. 82. This curve may be taken as representing the minimum nickel content of stably austenitic steels. Alloys with such a content of nickel, however, are rather hard and they work harden at an extremely rapid rate ; hence, in practice, it is usual to add more nickel than this minimum amount. The softening effect of this extra nickel is shown by comparing steels D and E in Table XXX. According to curve C, Fig. 82, steel D contains about the minimum amount of nickel necessary to produce fully austenitic material. The addition of a further 2 per cent., however, produces a markedly softer steel ; it also materially reduces the rate of work hardening, as is evident from a comparison of curves E and F in Fig. 88.

The physical properties of these austenitic steels depend on their composition and the mechanical and thermal treatment they have received. They thus possess a certain similarity with the martensitic steels but only in a very slight degree ; actually the heat treatment operations applied to the two types of steel are widely different and the possibility of modifying the properties of the steels by purely

* *Trans. Amer. Inst. Min. & Met. Eng.,* 1927, Vol. 75, p. 166.

heat treatment processes is very much less in the case of the austenitic than of the martensitic type. Thus the fundamental operation in the heat treatment of martensitic steels is the production of great hardness by cooling the steel more or less rapidly, depending on its composition, from some temperature above a certain minimum. The hardness thus produced may then be removed to a greater or less extent by tempering, and the two heat treatment operations combined suffice, within wide limits, to obliterate the effects of any prior treatment, both as regards hardness and structural condition. The steel, if previously soft, may be made hard and if previously coarse in structure, owing to overheating, may be refined. No similar series of changes may be produced in a fully austenitic steel. The latter cannot be hardened by any form of heat treatment ; it may only be hardened by mechanical work, but when so hardened it
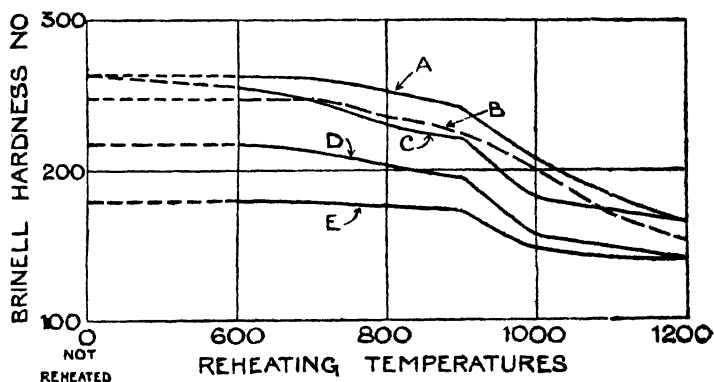
Fig. 91. Effect of re-heating to the temperatures indicated on the Brinell hardness values of hot rolled bars of austenitic steels.

Mark.	Carbon %	Chromium %	Nickel %
A.	0·23	20·5	6·64
B.	0·24	20·2	8·4
C.	0·12	18·0	8·2
D.	0·08	17·2	10·0
E.	0·08	15·4	10·7

may be softened by heating. Again, if the steel possesses a coarse structure, the latter can only be refined by mechanical work, followed in some cases by a suitable reheating ; it is not refinable by heat treatment only. It may, however,

be made coarse by overheating. The heat treatment operations of austenitic steels are thus quite different in type from those previously considered.

In order to study the effect of composition on the mechanical properties of austenitic steels, it is necessary that the several samples tested shall have received comparable treatment. For example, if rolled bars of about one inch in diameter are considered, these are almost certain to have been hardened, to some extent at least, by the rolling process, unless this has been conducted at a very high temperature. The effect of reheating rolled material to progressively higher temperatures may be illustrated by the curves in Fig. 91. These indicate that softening may commence in the neighbourhood of 700° C. and continue up to the highest temperatures short of melting. For various reasons, which will be considered presently, it is usual to soften these steels, after forging or rolling operations, by reheating them to some temperature in the range 1000° to 1200° or 1250° C. and cooling rapidly therefrom. An inspection of Fig. 91 shows that the lower temperature provides a suitable degree of softening for the steels containing about 15 or 16 per cent. chromium and 10 or 11 per cent. nickel, but that a temperature of about 1200° C. is necessary to obtain a comparable degree of softening in those of higher chromium and lower nickel contents. Actually, Messrs. F. Krupp recommend 1150°/1170° C. as a softening temperature for " V.2.A." and it is obvious that by so treating this material it is made considerably softer than if a reheating temperature in the neighbourhood of 1000° C. were employed. After being quenched from these high temperatures, the steels are exceedingly tough and ductile. They have a low yield point and one, moreover, which is often not well-defined ; its value, however, as ordinarily determined in tensile tests, is as a rule less than about fifteen tons per sq. inch. Tensile strength varies with composition and the temperature to which the steel has been finally reheated, but it is generally in the range 35/65 tons per sq. inch. Some typical mechanical properties obtained from a number of these steels, after reheating to 1000/1050° C. and quenching in water therefrom, are given in Table XXXIII, and a consideration of these indicates :—

(a) A high carbon content noticeably hardens the

steel, though its effect in this direction is probably not so great as in the martensitic steels.

(b) The higher the chromium content, other things being equal, the higher the tensile strength.

(c) The chief factor in influencing the tensile strength of the steels is the amount of nickel they contain in excess of that required to produce an austenitic steel, as indicated in curve C in Fig. 82. The action of this excess nickel has been referred to before in connection with the results given in Table XXX, page 150.

TABLE XXXIII.

Mechanical Properties of Austenitic Steels as affected by Composition.

Treatment : W.Q. 1000/1050° C.

Carbon %	Chromium %	Nickel	Yield Point, tons pe sq. inc	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinel Hard ness Numbe .	Izod Impact, ft. lbs.		
0·13	11·2	11·9	15·2	42·8	80·0	76·3	153	105	115	109
0·08	11·5	15·8	17·0	34·6	61·5	74·5	112	106	95	110
0·08	14·2	10·8	13·0	38·6	72·0	73·6	149	105	110	110
0·16	14·4	10·6	18·2	42·7	64·5	69·8	156	110	112	110
0·36	13·7	10·4		58·2	36·0	30·0	255	63	84	63
0·09	16·0	8·5	16·0	56·4	43·5	57·0	149	120	119	112
0·09	16·0	10·9	16·0	39·6	66·7	71·7	143	98	100	98
0·17	16·3	10·6	16·0	45·2	54·5	66·8	183	116	118	113
0·24	16·7	8·1	27·6	62·9	29·0	23·0	217	72	70	74
0·27	16·0	10·6	26·0	52·0	41·5	59·3	202	91	120	95
0·32	15·7	10·4	26·0	49·6	43·5	58·2	192	88	82	87
0·11	17·4	.7·6	14·0	63·2	46·0	54·6	179	112	118	112
0·09	17·2	10·9	14·8	46·0	66·0	66·8	146	106	110	108
0·12	18·0	8·2	16·8	54·8	56·0	58·2	163	120	120	118
0·08	18·0	10·5	18·0	38·4	73·0	75·4	153	106	100	102
0·23	17·2	10·9	—	47·1	45·5	61·5	207	111	108	108
0·23	20·5	6·64	25·5	67·0	48·0	39·7	196	107	120	120
0·24	20·2	8·4	27·0	53·0	59·0	51·4	185	118	120	120
0·22	23·1	9·0	28·0	50·8	43·0	49·7	196	46	48	50
0·11	21·8	10·8	21·0	39·6	55·0	64·7	166	100	100	105

When quenched from high temperatures, these steels consist entirely of austenite unless their carbon content be rather high, in which case some free carbide may be present as in Fig. 95. The minimum temperature required to produce this condition is about 1000° C. in the " Anka " type (15/16 per cent. chromium, 10/11 per cent. nickel) but rises with increasing chromium content, a 20 per cent. alloy requiring a temperature of about 1150° C. Once this com-

TABLE XXXIV.

Effect of Softening Temperature on the Properties of Austenitic Steels.

Mark.	Carbon %	Chromium %	Nickel %
A.	0·15	16·3	10·7
B.	0·09	16·0	10·9
C.	0·27	16·0	10·6
D.	0·12	18·0	8·2
E.	0·23	20·5	6·64
F.	0·24	20·2	8·4

Mark.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.		
A.	W.Q. 1000° C....	20·0	46·6	61·0	67·8	163	111	108	
	W.Q. 1350° C....	12·6	38·7	72·0	73·6	126	105	95	
B.	W.Q. 1000° C....	16·4	39·6	66·7	71·7	126	—		
	W.Q. 1150° C....	14·0	38·1	71·5	75·4	126	—		
	W.Q. 1300° C....	14·0	36·5	73·5	74·5	107	—		
C.	W.Q. 1000° C....	26·0	52·0	41·5	59·3	187	—		
	W.Q. 1150° C....	25·2	46·6	65·5	69·8	156	—		
	W.Q. 1300° C....	19·2	44·6	70·0	69·8	187	—		
D.	W.Q. 1000° C....	13·5	58·2	63·5	58·6	—	—		
	W.Q. 1100° C....	12·0	53·8	58·5	52·0	—	—		
E.	W.Q. 1050° C....	25·5	67·0	48·0	39·7	196	107	120	120
	W.Q. 1150° C....	18·0	51·7	67·0	60·4	170	110	110	110
F.	W.Q. 1050° C....	27·0	53·0	59·0	51·4	185	118	120	120
	W.Q. 1150° C....	19·2	47·0	67·0	68·8	166	97	107	108

Plate XIX

Fig. 92. "Anka" steel, 0·1 % carbon, 15·2% chromium, 11·4% nickel: W.Q. 1000 C × 300.

Fig. 93. "Anka" steel, 0·15% carbon, 16·3% chromium, 10·7% nickel: A.C. 1350°C × 50.

Fig. 94. "Anka" steel, as cast. × 12.

Fig. 95. Free carbide in a high carbon austenitic alloy containing 0·44% carbon, 20·0% chromium and 6·47% nickel, fully softened. × 300.

Plate XX

Fig 96. Fractured tensile test piece from " Anka " casting; this test piece gave 35·5% elongation in spite of its very coarse grain size.

pletely austenitic stage has been reached (a condition not produced after reheating to temperatures lower than those given above, as will be seen presently), the only effect of still higher quenching temperatures is the production of a coarser grain size. This may be illustrated by Figs. 92 and 93 in which are depicted the structures of " Anka " steel after reheating to 1000° C. and 1350° C. respectively; note that the magnification of the former photograph is six times that of the latter. Contrary to general experience with ordinary steels, however, coarse structures such as Fig. 93 do not make austenitic steels lose their great toughness ; as witness the results on steel A in Table XXXIV. At the same time there is no virtue in a coarse structure and its presence in these steels may be disadvantageous for other reasons, e.g., in material intended for cold pressing operations where a coarse grain size is likely to lead to a rough surface in a deeply pressed article, a feature common to many metals.

The remarkable toughness found in these steels even when excessively coarse grained has, however, at least one very decided advantage ; it enables one to produce castings possessing good mechanical properties. Steel castings, as a rule, are very coarse grained as cast ; in ordinary steels this structure can be refined to a very considerable extent by suitable heat treatment. Castings of the hardenable stainless steels are also refineable by similar means, though probably with greater difficulty than ordinary steels and not so efficiently. Castings of austenitic steels are, however, quite unrefineable by any heat treatment process, but nevertheless they give good figures for ductility and toughness as Table XXXV indicates. Tests A and B in this table were obtained from castings of considerable size and the coarse structure they possessed is evident from the appearance of part of the fractured test piece shown in Fig. 96, and the typical microstructure in Fig. 94. The latter also shows " coreing " effects, in the individual grains, due to selective freezing ; reference was made to a similar feature in chromium steels, on page 85.

Attention has been called to the low yield point value of austenitic steels. As ordinarily determined in tensile tests, a value of 15 tons per square inch, or less, is generally obtained from the completely austenitic material. The presence of free carbide in a sample may raise the observed

TABLE XXXV.

Mechanical Properties of " Anka " Castings.

No.	Carbon %	Chromium %	Nickel %
1	0·13	· 14·9	10·7
2	0·18	15·8	10;6
3	0·08	14·9	11·1
4	0·18	14·8	10·1

No.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Bend Test	Izod Impact, ft. lbs.		
1	As cast ...	12·0	31·2	51·0	45·9	—	180°	—		
2	,, ...	16·4	35·8	69·0	60·4	—	180°	98	102	
3	,, ...	—	29·2	35·5	36·4	—	180°	—		
{	,, ...	14·0	28·8	37·0	30·6	124	—	94	90	91
{	,, ...	15·6	30·6	44·0	47·2	116	—	85	89	89
{	W.Q. 1000° C....	15·7	30·0	38·0	35·0	118	—	91	98	100

value appreciably ; a higher value than 15 tons per square inch is given, for example, by material containing 20 per cent. chromium or thereabouts when quenched from 1000° C. or by steels of lower chromium content but containing 0·2 per cent. carbon or more when similarly treated. In both these cases, the microstructure shows the presence of much free carbide, a condition not always desirable from a corrosion resistance standpoint.

When loaded continuously for considerable periods, the austenitic steels yield slightly under still lower stresses ; movement can frequently be detected in this manner when the stress exceeds about ten tons per square inch. The stretch in such a case is only small and it is almost certainly not continuous ; the strain hardening due to this extension raises the yield point with the result that movement gradually diminishes and ultimately ceases.

These steels, as would be expected, have very low values for the limit of proportionality ; in the fully softened condition probably not more than five or six tons per square inch. In some cases, in fact, the load-extension diagram appears to be curved from the origin. As a result,

values for Young's modulus are likely to vary to some extent. The following data were obtained by Prof. Lea, of Sheffield University, on samples supplied by the author :—

Carbon %	Chromium %	Nickel %	Treatment.	Limit of Prop.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 4 ins.	Reduction of Area per cent.	Young's Modulus, lbs. per sq. inch.
0·12	15·8	11·2	W.Q. 1000° C....	4·0	13·5	38·4	58·0	71·0	$30·0 \times 10^6$
0·13	16·2	10·3	,, ...	5·0	12·5	38·9	57·0	69·0	$26·5 \times 10^6$
0·08	11·5	15·8	,, ...	3·5	11·0	34·8	53·0	73·2	$28·9 \times 10^6$
0·12	18·0	8·2	{ ,, ...	4·0	13·5	58·2	54·0	58·6	$28·9 \times 10^6$
			{ W.Q.1100°C....	3·5	12·0	53·6	50·0	52·0	$28·5 \times 10^6$

Dr. Hatfield* found the Young's modulus of " Staybrite " to lie between $26·5 \times 10^6$ and $28·8 \times 10^6$ pounds per square inch, with a mean value of $27·7 \times 10^6$.

(4) EFFECTS OF REHEATING AUSTENITIC STEELS IN THE RANGE 500°/900° C.

It has been claimed on more than one occasion that one of the great virtues of the austenitic type of non-corrosive steel is that its structure is stable during or after reheating to high temperatures. Such steels have no carbon change point and are not subject to tempering ; hence, it is stated, the structure they possess when first put into service, presuming, of course, they have not been cold worked, does not change even though that service involves heating repeatedly, or for long periods, to temperatures reached by superheated steam or to still higher temperatures.

There is, of course, a considerable measure of truth in this ; the grains of austenite which form, with the exception of non-metallic inclusions, the whole of the structure of the fully softened material may, and in many cases do, remain austenite, i.e., they do not change to any other constituent after reheating to any temperature short of melting. But it is not the whole truth. When these austenitic steels are reheated in the range 500°/900° C., even for very short periods, they undergo a structural change which, though small, has very pronounced effects on the resistance of the material to many forms of chemical attack. This structural change consists in the precipitation of carbide as fine particles, very frequently forming a network round the grains of

* Private communication.

austenite which make up the bulk of the structure. This
precipitation takes place so rapidly that a heating of only
a few minutes duration in this temperature range will suffice
to bring it about. Figs. 97 and 98 show typical structures
of material treated in this manner. They are interesting in
that they were produced by taper heating a small bar of the
steel in a manner intended to reproduce the conditions
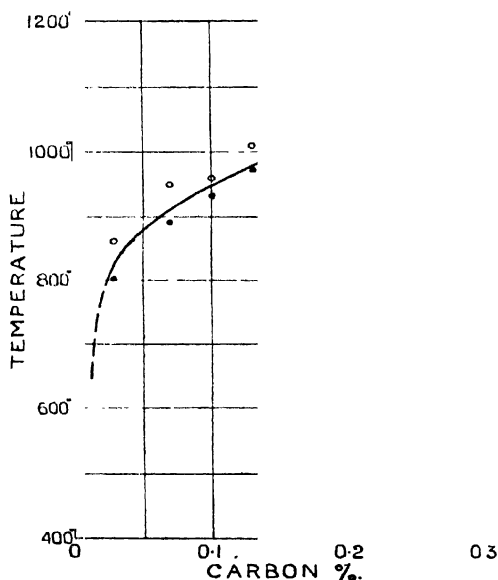
Fig. 99. Solubility of carbon in steel containing 18% chromium and
8% nickel (Bain and Aborn).

obtaining in welding operations. One end of this small bar
was heated to its melting point by means of an
oxy-acetylene torch. The operation required only a few
minutes and the bar was then quenched rapidly in water.
On preparing the bar as a microsection and etching with
a 10 per cent. solution of hydrochloric acid in alcohol, it
was noticed that the narrow band, which had been reheated
to a dull red heat, etched very quickly as compared with
the hotter and cooler parts of the bar. The grain boundaries
in this narrow band were easily visible after an etching

Plate XXI

FIG. 97. "Anka" steel, 0 1% carbon.
15 16% chromium, 10 11% nickel, after
heating for about two minutes at 700°C,
lightly etched. × 150.

FIG. 98. "Anka" steel, 0 1% carbon,
15 16% chromium, 10 11% nickel: after
heating for about two minutes at 700°C.
lightly etched × 750.

period of ten or fifteen minutes, as indicated in Fig. 97, although by that time the structure of the remainder of th e bar was only faintly visible. The reason for the rap id appearance of these grain boundari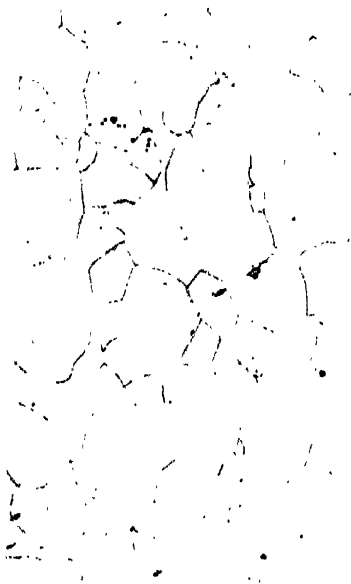es is due to the fact th at they are occupied by a thin film of carbide, a feature mo re easily visible in Fig. 98, taken at a much higher magnificatio n. In this photograph the film is not quite continuous and t he relative invisibility of the grain boundary, where no film is present, is striking.

The rapid precipitation of carbide from austenite m ay occasion some surprise, particularly as one of the featur es which distinguish this constituent from ferrite is its pow er of dissolving carbon. Experiment indicates, however, th at the solubility of carbon in these austenitic chromium-nick el steels varies with temperature and is very small belo w 900° C. Recent investigations by Bain and Aborn* sho w that the relation between temperature and solubility is a s indicated in Fig. 99. In the experiments to which this diagram relates, samples of steels of different carbon contents, quenched from various temperatures, were examined micro-scopically. Those quenched as indicated by the small circles in Fig. 99 were free from carbide, but the latter was distinguishable in experiments represented by small dots. The curve indicates that less than 0·03 per cent. carbon is soluble at temperatures below 800° C.

Reference may usefully be made here to the behaviour of steels containing less nickel than is necessary to give a stably austenitic structure. It will be observed from curve A, Fig. 85, and curve D, Fig. 87, that after such steels have been made austenitic by quenching from high temperatures, they harden to a considerable extent on being subsequently reheated in certain ranges of temperature below 900°/950° C. It will be noticed from Fig. 99 that the solubility of carbon becomes appreciable at this temperature (900°/950° C.) above which the acquired hardness is reduced. One may suppose that on reheating the austenitic forms of such steels in the range of temperature producing hardness, there is not only a precipitation of carbide but also a change, more or less complete, of the austenite into martensite. One can conceive that such steels remain austenitic after cooling rapidly from a high temperature because, the whole of the

* "The nature of the Nickel-Chromium Stainless Steel." *A.S.S.T.*, Sept., 1930.

carbide having then dissolved, there is sufficient chromium, nickel and carbon in solution to make the austenite existing at the high temperature stable during the subsequent rapid cooling. On reheating this austenite to lower temperatures, however, part of the carbon and chromium fall out of solution, as chromium carbide, and the remaining austenite is not then sufficiently rich in these elements and nickel to be stable during cooling. Hence it·changes more or less completely to martensite, with consequent hardening of the steel.

It appears reasonable to assume that in the steels regarded as stably austenitic, the austenite grains still retain sufficient chromium, carbon and nickel in solution to make them stable despite the precipitation of chromium carbide which takes place during reheating in the " dangerous" range—for so may this range of 500°/900° C. be described owing to its effect on the resistance to corrosion of the steel. If this be correct, a steel which contains a considerable excess of nickel, over that necessary to make it austenitic, is likely to be less affected in its mechanical properties by heating in this " dangerous " range than one which contains only a little more than this minimum amount.

Actually the effect on the mechanical properties of steels of the " Anka—Staybrite—V.2.A." type produced by reheating for short periods to temperatures between 500° and 900° C. is very slight, as is indicated by the results in Table XXXVI. But when similar steels are treated at these same temperatures for prolonged periods the effects are more noticeable, see Table XXXVII, suggesting that the precipitation of carbide, though commencing very rapidly, requires a considerable time for its completion. Further, the more complete precipitation of the carbide reveals differences in the steels not apparent in the shorter period tests. Thus the most noticeable features of the results in Table XXXVII are the very considerable drop in impact value of the higher chromium steel " S " and the fact that the tensile test result of the bar treated at 700° C. has all the characteristics of a hardened and tempered, instead of an austenitic, steel. Thus its yield point value is very high and its general elongation, apart from the local necking at the fracture, is quite low ; the steel in fact appears to have lost quite considerably its austenitic character. The " Anka "

TABLE XXXVI.

Effect of Reheating in the Range 700°/900°C. on Mechanical Properties.

Mark.	Carbon %	Chromium %	Nickel %	Previous Treatment. %
A.	0·15	15·7	10·7	W.Q. 1100°C.
S.	0·09.	16·1	8·5	W.Q. 1100°C.

Mark.	Treatment.	Yield Point. tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of area per cent.	Brinell Hardness No.	Izod Impact, ft. lbs.
A.	Not reheated	16·7	43·7	74·0	74·5	153	107 120 116
	Reheated 700°C. for 30 mins.	17·2	44·1	74·0	69·8	163	113 112 —
	,, 800°C. ,, ,,	15·8	44·1	71·0	68·8	170	100 110 111
	,, 900°C. ,, ,,	15·8	44·1	69·0	66·8	163	105 97 106
S.	Not reheated	12·2	60·2	50·0	51·0	156	120 115 120
	Reheated 700°C. for 30 mins.	13·8	61·0	45·0	45·9	166	101 104 115
	,, 800°C. ,, ,,	13·8	60·2	47·0	49·7	170	91 103 120
	,, 900°C. ,, ,,	12·8	60·2	45·0	45·9	163	103 104 114

TABLE XXXVII.

Effect of Prolonged Heating in the Range 500°/900°C. on Mechanical Properties.

Mark.	Carbon %	Chromium %	Nickel %	Previous Treatment. %
A.	0·11	15·7	10·5	W.Q. 1000°C.
S.	0·10	17·2	7·9	W.Q. 1100°C.

Mark.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of area per cent.	Brinell Hardness No.	Izod Impact, ft. lbs.
A.	Not reheated	14·0	42·0	60·0	70·7	156	119
	Reheated 500°C. for 1 week...	20·0	46·0	64·0	75·5	163	94
	,, 700°C. ,,	14·0	47·0	41·0	62·2	170	92
	,, 900°C. ,, ...	18·4	46·0	59·5	65·8	159	50
S.	Not reheated	16·0	59·3	44·0	53·4	170	109
	Reheated 500°C. for 1 week	21·0	64·6	47·0	56·6	179	30
	,, 700°C. ,,	48·0	60·8	21·0	52·2	269	41
	,, 900°C. ,,	18·0	64·4	29·0	52·2	179	24

type of steel, which owing to its higher nickel content is more stably austenitic, is much less affected by the prolonged heatings, though such changes as are produced in it tend in the same direction as in the " Staybrite " steel.

The microstructure of these samples which had been reheated for a week contained very much free carbide, as is evident from Figs. 100 to 102. It seems probable that the precipitation of this carbide has displaced the composition of the remaining austenite grains towards curve B in Fig. 82. As a result steel S has partially reverted to the martensitic type ; steel A, on the other hand, contains more " excess " nickel (see page 158) and hence has remained austenitic. The fact that the network and particles visible in Figs. 97, 98 and 100 to 102 really consist of carbide may be proved by repolishing the sections and re-etching them with Murakami's reagent, which darkens the carbide but leaves the rest of the structure unattacked, see Fig. 103.

Although the effect of these carbide films on the mechanical properties may not be great even after prolonged soaking and is generally negligible after short reheatings, their presence may be completely disastrous from a corrosion resisting point of view. This aspect of the matter and also that of the use of the steels for continuous service in this range of temperature will be dealt with in later chapters.

Not only are the carbide films produced by reheating the steels in the range 500°/900°C., but they also form during slow cooling through this range from higher temperatures. For example, structures quite similar to Figs. 97 and 98 were obtained by merely checking the air cooling of small samples for twenty minutes at 500°, 600°, 700° and 800°C. during cooling from 1,000° or 1,200°C. Consequently the steels should always be rapidly cooled, e.g., by quenching in water or oil or, if of very small size, cooling freely in air, from 1,000°/1,200°C. for their final heat treatment operation. The necessity for rapid cooling must be emphasised ; thus the rate of cooling produced by allowing a bar 1 inch in diameter to cool freely in the air from the necessary softening temperature (e.g., 1,000°/1,200°C.) is not sufficiently fast to prevent the formation of intergranular carbide films in many of these steels.

The precipitation of carbide during even moderately slow cooling from 1,000°C. or over, restricts the use of forged .

Plate XXII

Fig. 100. "Anka" steel, 0·11% carbon, 15·7% chromium, 10·5% nickel, heated at 500°C. for 7 days; etched 10% hydrochloric acid in alcohol. × 750.

Fig. 101. "Anka" steel, 0·11% carbon 15·7% chromium, 10·5% nickel, heated at 700°C. for 7 days; etched 10% hydrochloric acid in alcohol. × 750.

Fig. 102. "Anka" steel, 0·11% carbon, 15·7% chromium, 10·5% nickel, heated at 900°C., for 7 days; etched 10% hydrochloric acid in alcohol. × 750.
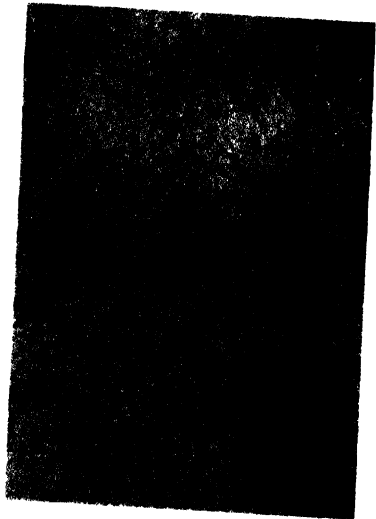
Fig. 103. "Anka" steel, 0·11% carbon, 15·7% chromium, 10·5% nickel, heated at 800°C., for 7 days; etched Murakam's reagent. × 750

Plate *XXIII*

Fig. 104. "Anka" steel, 0·14% carbon, 14·9% chromium, 10·8% nickel, rolled at 800 C.; showing carbide films; etched 10% hydrochloric acid. × 100.

To face page 171.]

Fig. 105. "Anka" steel, 0·14% carbon, 14·9% chromium, 10·8% nickel, rolled at 800 C.; showing carbide films; etched 10% hydrochloric acid. × 750.

or rolled material without subsequent heat treatment. The fact that rolled bars of small size are hardened to some extent by the rolling operation has been mentioned before. The mechanical properties of such bars, the rolling of which was completed at a temperature not lower than about 900°C., are given in Table XXXVIII along with the results obtained on the same bars after softening. The properties of the rolled material are interesting to the engineer, particularly on account of higher yield point value as compared with heat treated material. This value may indeed be raised quite considerably by using still lower rolling temperatures, as is evident from the tests in Table XXXIX. Unfortunately however, the use of these low rolling temperatures involves the material being held for quite an appreciable interval in the " dangerous " range and as a result the structure of bars so treated contains quite noticeable films of carbide, even though they were reheated, prior to rolling, to a sufficiently high temperature to produce the completely austenitic condition. This for example was the case in the experiments summarised in Table XXXIX, but the structure of bar F, the finishing temperature of which was 780°C., disclosed the presence of much carbide as is evident from Figs. 104 and 105. One may also notice the pronounced distortion of the grains in these photographs.

TABLE XXXVIII.

Comparison of Rolled and Heat-treated Bars of Austenitic Steels.

Carbon %	Chromium %	Nickel %	Size of Bar.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness No.	Izod Impact, ft. lbs.
0·10	15·2	11·4	1⅛″	Rolled ...	28·0	43·6	51·0	67·8	202	113
			,,	W.Q. 1000°C.	19·1	38·9	70·0	72·6	137	107
0·10	15·0	9·0	⅞″ 1¼″	Rolled ...	33·4 26·8	70·7 68·0	45·0 43·0	59·7 49·7	241 212	120 120
			,,	W.Q. 1000°C.	16·4	58·9	57·0	51·0	163	118
0·21	15·4	10·3	1″	Rolled ...	36·5	54·7	43·0	55·8	—	108
			,,	W.Q. 1000°C.	18·8	45·7	64·0	67·8	163	116
0·24	20·2	8·4	1″	Rolled ...	43·8	59·8	37·3	53·0	248	68
			,,	W.Q. 1050°C.	27·0	53·0	59·0	51·4	185	119

It follows from this that bars or forgings should not be used in the rolled or forged condition unless these opera-tions can be so controlled that they are completed before the steel has cooled below about 950°C., so that the forged or rolled product may then be rapidly cooled. The use of bars with a high yield point value obtained by deliberate rolling at low temperatures, as those in Table XXXIX, is very undesirable, as it is extremely likely to·lead to disastrous corrosion troubles. A similar remark applies to attempts to use partially softened material produced by reheating work hardened bars in the range 700°/900° C. (see Fig. 91).

TABLE XXXIX.

Effect of Rolling Temperature on the Mechanical Properties of " Anka."

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·14	0·12	0·20	14·9	10·8

·1$\frac{3}{4}$″ sq., bars rolled to 1$\frac{1}{8}$″ sq. The 1$\frac{3}{4}$″ bars were heated to 1150° C. prior to cooling to and rolling at the temperatures given.

Mark.	Temperature of Rolling.		Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Brinell Hard-ness Number.	Izod Impact, ft. lbs.
	Be-ginning.	End.						
A.	1150°	1000°	18·7	43·3	57·5	67·8	179	116 115
B.	1000°	950°	20·7	43·9	55·0	67·8	179	—
C.	950°	930°	22·6	43·1	52·5.	61·5	187	—
D.	900°	850°	25·6	47·5	50·0	65·8	217	—
E.	850°	800°	26·6	47·1	49·5	64·8	223	—
F.	800°	780°	35·4	47·7	45·0	66·8	223	116 116

In all the tests given for the austenitic steels, it will·be noted that the ratio of tensile strength (expressed in tons per square inch) to Brinell hardness number differs appreciably from that found for the hardenable stainless steels or for the general run of carbon or alloy steels. For the latter, the ratio has a value varying between 0·22 and 0·24. In the

case of the austenitic steels it has a much higher value, sometimes reaching 0·35 ; and moreover, it varies to a greater extent than with ordinary steels.   Owing to the relatively constant value of the ratio, in the case of ordinary steels, the Brinell hardness value has been widely used in estimating the tensile strength of these steels, but it should be used with considerable caution for the same purpose in connection with austenitic steels.   If the ordinary figures applicable to most steels are used, the calculated value of the tensile strength so found from the Brinell hardness number, will be less than that actually obtained from a tensile test by an amount which varies with the condition of the steel.   As a general rule, the difference is greater when the material is in its softest condition and less when it is more or less work hardened ; it is also likely to be greater with a steel which contains little more than sufficient nickel to make it austenitic than with one containing two or three per cent. more than this minimum amount, because the former steel work-hardens at a considerably faster rate than the latter.

(5)   EFFECT OF COLD WORK ON AUSTENITIC ALLOYS.

The effects of cold work on austenitic steels have some extremely interesting features.   Their higher rate of work-hardening has already been referred to in relation to the effect of nickel on steels containing 20 per cent. chromium (page 155), but as this point is rather important, it may not be out of place to dwell on it to some extent as thereby disappointment in the use of the material for cold-working operations may be avoided.

The fact that these steels give very high values for elongation per cent. in tensile tests and have also a comparatively low yield point, has been adduced as evidence of great capacity for undergoing deformation when cold-worked. This is quite correct, and one of the features of the steels is their capability of being pressed, in the form of sheet, into a variety of shapes.   But it should also be borne in mind that the type of tensile test obtained indicates that the material hardens considerably as a result of cold work.

Typical load extension diagrams obtained from tensile tests on a stainless iron and an austenitic steel are reproduced

in Fig. 106. Each test-piece commenced to extend plastically at its yield point and the fact that it was able afterwards to carry a still greater load, despite its diminishing cross-sectional area, shows that the material hardened as a result of this plastic flow and thus required a higher stress to induce further flow. At the maximum load, the test-piece commenced to neck, owing to the rate of reduction of cross-sectional area becoming greater than the rate of increase in hardness in the steel. Whereas, however, the stainless iron reached its maximum load after its cross-sectional area had been reduced some 15 per cent., the austenitic steel continued to extend 45 or 50 per cent. before necking commenced. The difference between the two steels is shown strikingly by calculating the stress at maximum load in terms of cross-sectional area of the test-piece at that moment. These figures are 46·5 and 66·0 tons per square inch for the stainless iron and austenitic steel respectively.
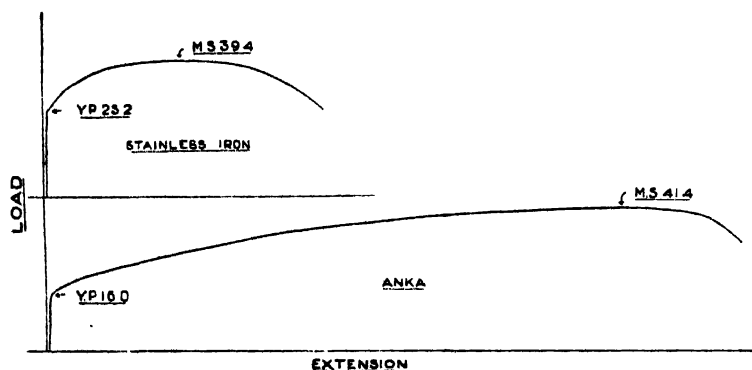
FIG. 106. Load-extension diagrams of stainless iron and "Anka" steel.

The behaviour of these test pieces would lead one to suspect that when these austenitic chromium-nickel steels, such as " Anka," " V.2.A." or " Staybrite," are cold-worked, they would flow very easily at first, considerably easier, for example, than stainless iron with its higher yield point, but as the degree of cold work increases they would stiffen up much more rapidly than the stainless iron so that samples which had to be heavily cold-worked without intermediate annealing would be expected to require considerably heavier pressure or blows to perform this operation than, for example, similar pieces of stainless iron.

Actually this is found to be the case, and to give some concrete expression to this hardening effect, one may compare the behaviour of small cylinders of " Anka " steel and stainless iron when being compressed cold.   Fig. 107 gives the relationship between load and reduction in height of small cylinders (0·06 in. long and 0·535 in. diameter) when compressed under steadily increasing loads and indicates that while the " Anka " cylinder lost height under small
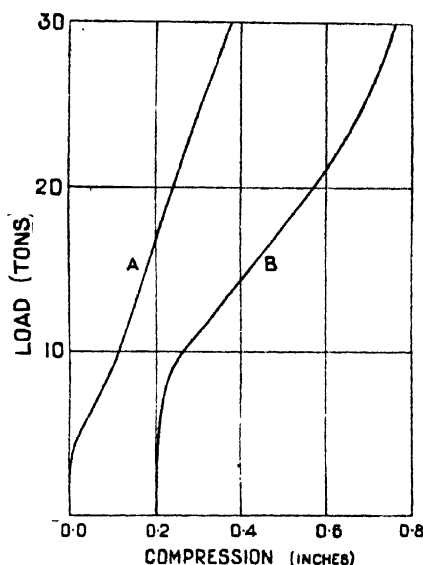
FIG. 107.   Compression tests on " Anka " steel (A) and stainless iron (B).

loads at a greater rate than the stainless iron, thus under a load of 10 tons the former was reduced 14·5 per cent. and the latter 7·45 per cent., the relative rates changed greatly as the load increased, so that with a load of 80 tons the " Anka " was reduced only 41·4 per cent., the corresponding figure for the stainless iron being 58·4 per cent.

These figures provide an explanation of what has been found in certain cases in practice.   Thus experience has shown that cold riveting operations are much more easily · carried out with stainless iron than with the austenitic steels.

When rivets are being closed, those made of the latter material flow easily at first but stiffen up under the operation so that the final forming of the head is more difficult than if rivets of stainless iron are used.

While, however, one may say quite correctly that the steels of the austenitic group as a whole work-harden at a faster rate than the stainless irons, they vary considerably among themselves, some of them hardening at a much faster rate than others. Evidence of this was given on page 155,
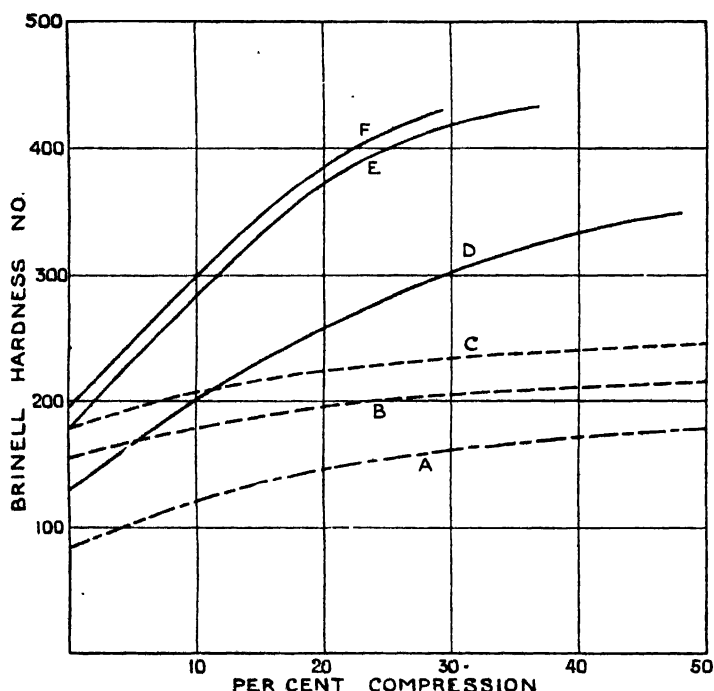
Fig. 108. Work hardening tests; relation between hardness and degree of compression.

A. Nickel Silver.
B. Mild Steel, 0·15 per cent. carbon.
C. 0·1 per cent. carbon, 13·5 per cent. chromium, 0·27 per cent. nickel.
D. 0·09 ,, ,, 16·0 ,, ,, 10·9 ,, ,,
E. 0·12 ,, ,, 18·0 ,, ,, 8·2 ,, ,,
F. 0·23 ,, ,, 20·5 ,, ,, 6·64 ,, ,,

where the effects of adding nickel to steel containing twenty per cent. chromium were discussed. It is also clearly shown in Fig. 108, in which are plotted the results of compression

tests on various types of austenitic material commercially available. For comparision, results similarly obtained on stainless iron, mild steel and annealed nickel silver (as being typical of material much used for cold pressing operations) are included. The austenitic alloys used for these tests had all been softened by water quenching from 1,000°C.; some of them may be obtained in a softer condition
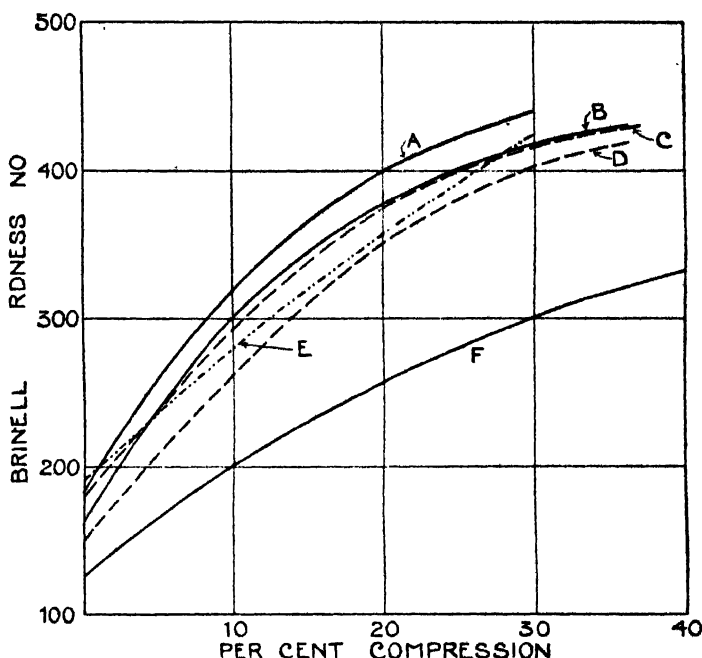
Fig. 109. Work hardening tests ; effect of softening temperature.

Curve.	Carbon %	Manganese %	Chromium %	Nickel %	Softening Temperature.
A.	0·11	0·17	17·4	7·6	1,000° C.
B.	,,	,,	,,	,,	1,100° C.
C.	0·12	0·15	18·0	8·2	1,000° C.
D.	,,	,,	,,	,,	1,100° C.
E.	1·2	12·4			1,000° C.
F.	0·09	0·17	16·0	10·9	1,000° C.

by quenching from higher temperatures, but the rate of work-hardening is not thereby reduced. For example, the results obtained from two steels of the "Staybrite" type are plotted in Fig. 109 ; in each case the use of 1,100°C. as a quenching temperature has lowered the initial Brinell

hardness number, but the curve obtained from the softer material runs, in each case, parallel to that from the same steel softened at 1,000°C.   Curves from an " Anka " steel and also from a typical " Manganese " steel are included ; that of the latter is especially interesting as it shows that this material hardens at a rate very similar to that of " Stay-brite."

Again, the presence of a carbon content somewhat higher than is usually present in these steels, hardens them appreciably.   In this case also the use of a higher softening temperature than 1,000°C., produces a distinct lowering of the hardness of the steel.   Fig. 110 illustrates this but also
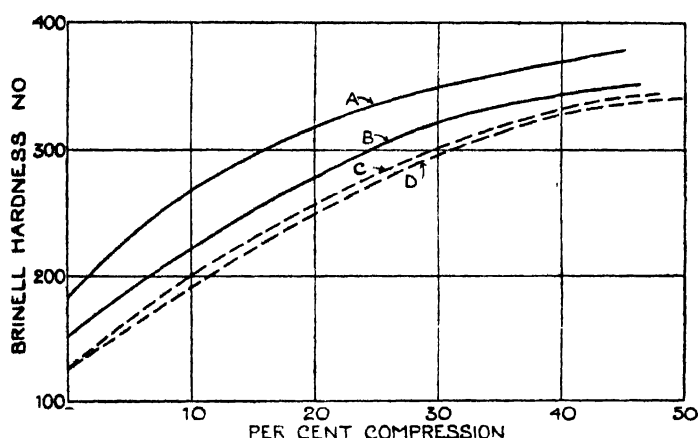
FIG. 110.   Work hardening tests ; effect of carbon content.

Curve.	Carbon	Chromium	Nickel	Softening
	%	%	%	Temperature.
A.	·27	16·0	10·6	1,100° C.
B.		,,	,,	1,150° C.
C.	·09	16·0	10·9	1,100° C.
D.				1,150° C.

shows that again the rate of work-hardening is not appreciably altered.   It is also evident from this diagram that 1,000°C. is adequate as a softening temperature for a normal " Anka " steel, containing 0·15 per cent. carbon or less.

From the point of view of the user who wishes to cold-work these alloys in various ways and who has probably machines of strictly limited power at his disposal, the loads necessary to produce similar amounts of deformation in the various steels are of paramount importance.   Fig. 111

supplies this information and indicates the much greater
· ease with which some of the steels may be compressed as
compared with others. For comparison, results obtained
on stainless iron, mild steel and annealed nickel silver are
again included.
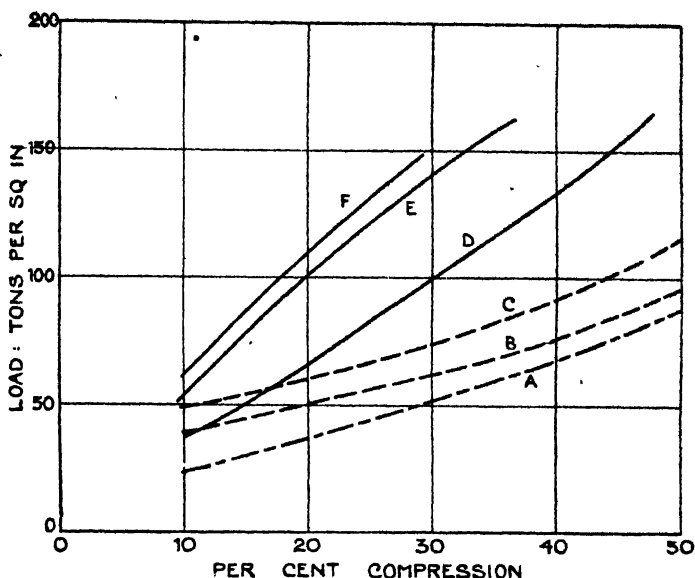
FIG. 111. Work hardening tests; loads necessary to produce stated
amounts of compression.

A. Nickel Silver.
B. Mild Steel, 0·1 per cent. carbon.
C. 0·01 per cent. carbon, 13·5 per cent. chromium, 0·27 per cent. nickel.
D. 0·09 „ „ 16·0 „ „ 10·9 „ „
E. 0·12 „ „ 18·0 „ „ 8·2 „ „
F. 0·23 „ „ 20·5 „ „ 6·64 „ „

A study of Figs. 108 to 111 indicates that the softest
austenitic steel, of those described, is the " Anka " type,
containing 15/16 per cent. chromium and 10/11 per cent.
nickel, with low carbon. But even this is distinctly harder
than, for example, nickel silver. This causes no great
difficulty if the machines used for cold-working operations
have a good reserve of power, but many existing machines
have been designed to deal with very soft metals, copper,
brass, nickel-silver and the like, and when these machines
are used for the austenitic stainless steels, some modification

of the operation may be necessary for the softest " Anka "
and still more so for the harder " Staybrite " steels.   The
results of efforts to produce still softer austenitic alloys,
which may be more amenable to certain commercial cold-
working operations, for example in the production of spoons
and forks and other household utensils, are illustrated in curves
A and B, Fig. 112.   For comparison, curves C and D
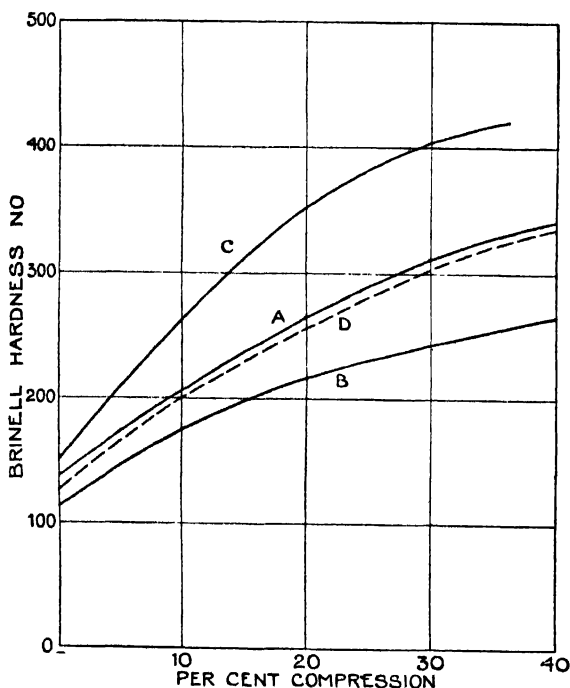
FIG. 112.   Work hardening tests ; special soft alloys.

Curve.	Carbon %	Chromium %	Nickel %	Softening Temperature.
A.	0·13	11·2	11·9	1,000° C.
B.	0·08	11·5	15·8	1,000° C.
C.	0·12	18·0	8·2	1,100° C.
D.	0·09	16·0	10·9	1,000° C.

refer to the standard " Staybrite " and " Anka " materials.
For many household (and other) purposes, a chromium
content of 12 per cent., or thereabouts, is sufficient to ensure
adequate resistance to corrosion ; to this lower chromium
content as well as to their higher content of nickel is due the

greater ease of working steels A and B as compared with C and
.D respectively.   The loads required to compress these four
steels are plotted in Fig. 113 and an inspection of these curves
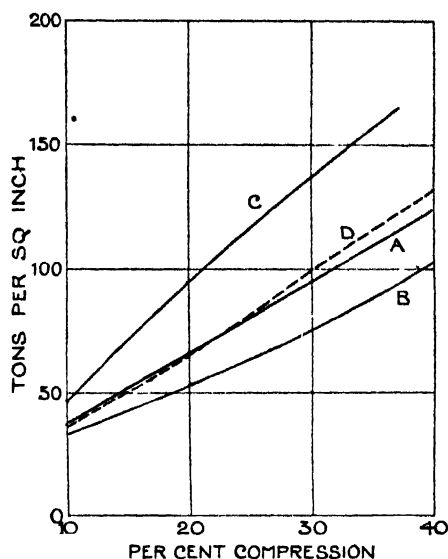
FIG. 113.   Loads necessary to compress steels.

Curve.	Carbon %	Chromium %	Nickel %	Softening Temperature.
A.	0·13	11·2	11·9	1,000° C.
B.	0·08	11·5	15·8	1,000° C.
C.	0·12	18·0	8·2	1,100° C.
D.	0·09	16·0	10·9	1,000° C.

shows that, when using machines of limited power, the degree
of deformation possible at one operation varies considerably
among the four steels.

In passing, it may be noted that the capacity of the
austenitic steels for hardening rapidly when cold-worked
accounts for the ratio between tensile strength and Brinell
hardness number of these steels being greater than it is for
other steels.   The degree of cold working produced in the
Brinell test is relatively less than in the tensile test and hence
the greater hardening effect produced in the latter raises the
ratio $\dfrac{\text{Tensile strength}}{\text{Brinell number}}$ of the austenitic steels and often to a
considerable extent, as was noted on page 172.   Incidentally
it may be observed that the value of this ratio gives an

approximate idea of the work-hardening capacity of the
steel.   The higher this ratio is, the more rapidly the material
will harden by cold work.   Other things being equal, there-
fore, a steel with as low a value as possible for this ratio
should be selected for cold-working operations ; if this low
value is also associated with a low value for the tensile
strength of the material, so much the better.

There is also another interesting peculiarity of the
austenitic steels and one which suggests that the effects
produced on them by cold-working are not independent of the
rate of application of the load.   It is known that values
obtained for the tensile strength of ordinary carbon steels,
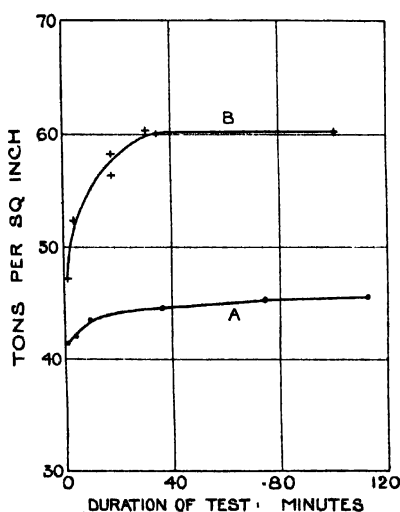
Fɪɢ. 114.   Effect of duration of test on value obtained for tensile strength.

Curve.	Carbon %	Chromium %	Nickel %
A.	0·15	15·7	10·7
B.	0·09	16·0	8·5

and also alloy steels of the hardenable type, are practically
unaffected by the rate at which the tensile test piece is
loaded.   This does not apply to the austenitic steels; the
value obtained for their tensile strength is lower, the more
rapidly the piece is elongated.   Results obtained from two

steels are plotted in Fig. 114, and from this it would appear .that this feature of austenitic steels is not unrelated to the rate at which they harden when cold-worked ; the faster this rate, the greater the effect of variations in the pulling speed on the value obtained for tensile strength.
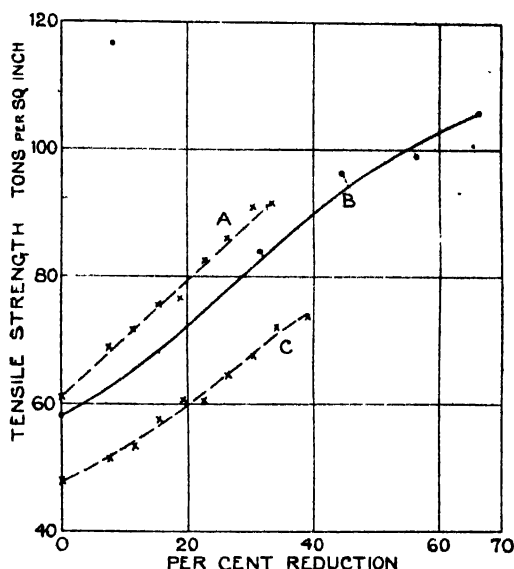
FIG. 115.   Tensile strength of cold-drawn wire and cold-rolled strip.

Curve.	Form.	Carbon %	Chromium %	Nickel %	Previous Treatment.
A.	Strip.	0·10	17·1	8·1	A.C. 1,050° C.
B.	Wire.	—	15·0*	10·0*	A.C. 950° C.
C.	Strip.	0·15	15·7	10·65	A.C. 1,050° C.

' Approximately.

As a result of the rapid rate of work-hardening of the austenitic steels, it would be expected that the increase in tensile strength, produced by drawing wires of this material definite amounts, would be greater than in the case of the ordinary stainless irons and steels.   A comparision of the slope of the curves in Figs. 78 and 115 shows that this is the case ; the latter diagram also indicates that wire and strip of high tensile strength may be obtained from the austenitic steels.

Details of tensile and bend tests on the strips whose

maximum stress values are plotted in Fig. 115 are given in Table XL. Both these and the results in Table XLI, relating to bright drawn bars, show that austenitic steels possess good ductility and toughness even when cold-worked considerably.

Work-hardened samples of austenitic steels, on being reheated to a series of gradually increasing temperatures,

TABLE XL.

Mechanical Properties of Cold Rolled Strip.

	Carbon %	Chromium %	Nickel %	Initial Thickness.
A.	0·15	15·7	10·6	0·132″
B.	0·10	17·1	8·1	0·132″

	Condition.	Per cent. reduction.	Proof Load.	Maximun Stress, tons per sq. inch.	Elongation per cent. on 4 ins.	Brinell Hardness Number.	Bend Test.	Reverse Bend.
A.	A.C. 1050°C.	nil	21·9	47·6	51·5	149	180° over 2T.	3
	Cold Rolled	7·7	38·2	51·5	37·0	228	,,	3½
	,, ,,	11·5	43·0	53·2	32·0	245	,,	2½
	,, ,,	15·4	50·3	57·6	25·0	269	,,	2
	,, ,,	19·2	52·3	60·6	22·5	277	,,	1½
	,, ,,	22·7	54·0	60·4	20·0	298	,,	2
	,, ,,	26·5	60·3	64·5	16·0	298	,,	1½
	,, ,,	30·3	64·6	67·4	11·0	302	180° over 2½T	½
	,, ,,	34·1	66·0	72·1	9·5	321	180° over 3T.	
	,, ,,	39·3	71·9	73·8	9·0	321	,,	
B.	A.C. 1050 ...	nil	19·2	61·2	60·0	149	180 over 2T.	3
	Cold rolled	7·7	30·3	68·9	45·0	228	,,	2
	,, ,,	11·5	39·2	71·4	36·5	262	,,	1
	,, ,,	15·4	45·0	75·5	35·0	298	,,	2
	,, ,,	19·0	50·3	76·5	31·5	302	,,	½
	,, ,,	22·7	60·5	83·0	26·0	340	180° over 2T cracked	½
	,, ,,	26·5	69·0	86·1	23·0	364	180° over 2T broke	0
	,, ,,	30·3	78·0	90·8	19·0	387	150° over 7T. cracked.	
	,, ,,	33·3	84·7	91·4	16·0	375	180° over 6T. broke.	

TABLE XLI.

Mechanical Properties of Bright Drawn " Anka " Rods.

Mark.	Carbon %	Chromium	Nickel %
A.	0·14	14·9	10·8
B.	0·09	17·0	10·4

Mark.	Original Size.	Condition.	% Reduction.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. nch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Izod Impact, ft. lbs.		
A.	¾″	W.Q. 1000°C.	nil	20·1	44·2	62·5	69·9	120	120	120
		Bright drawn	8·1	37·4	51·6	50·0	62·2	97	99	99
		,, ,,	15·9	51·0	58·2	37·0	61·5	43	49	47
A.	½″	,, ,,	12·0	41·6	53·1	50·0	66·8	69	72	71
		,, ,,	23·2	52·0	63·2	33·0	62·1	89	87	87
B.	1⅛″	W.Q. 1000°C.	nil	18·0	43·0	57·0	67·8	106	110	108
		Bright drawn	5·7	26·8	46·3	48·0	63·6	95	101	99
		,, ,,	10·0	33·4	51·3	47·0	63·6	92	101	101

behave in a similar manner to other work-hardened metals. Their hardness is practically unaffected by reheating to any temperature below a certain value characteristic of the metal, though not independent of the amount of cold work the latter has received ; reheating to higher temperatures than this value produces a more or less rapid fall in the hardness. In the case of the austenitic chromium-nickel steels, this critical temperature occurs in the range 500°/600°C.; its position, however, depends probably on the actual composition of the steel and certainly on the degree of cold-working to which the latter has been submitted ; severely cold-worked materials may commence to soften at temperatures somewhat lower than 500°C.

If a series of cylindrical samples of one of these steels be hardened by compressing them definite amounts, and the individual samples be then reheated to various temperatures up to 1,100°C., the Brinell hardness values of these reheated samples plotted against their respective reheating temperatures will give curves of the type shown in Fig. 116. These curves possess a notable feature ; the softening appears to take place in two stages, one commencing at 500°/600°C. and.

the other at 800°/875°C. It seems very probable that the retardation of the rate of softening as the temperature rises. between 600° and 800° or 850°C. is due to the precipitation of carbide as a network round the grains of austenite. Such a network of hard material (and all carbides in steel are hard
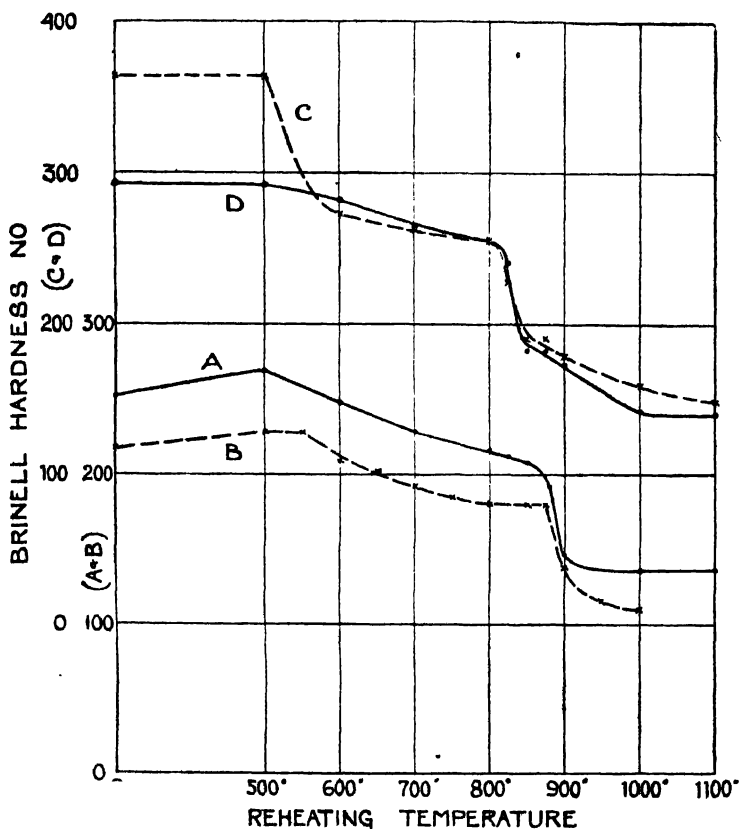
FIG. 116. Effect of re-heating to the temperatures indicated on hardness of cold-worked steels.

Curve.	Carbon %	Chromium %	Nickel %
A.	0·13	11·2	11·9
B.	0·08	11·5	15·8
C.	0·12	18·0	8·2
D.	0·16	16·0	11·2

substances) is likely to stiffen the structure and hence counter-act in some measure the loss in hardness which might be expected to occur as the reheating temperature rises above

600°C.   At 900°C. the carbide films have "balled up" appreciably (see Fig. 102, page 170) and hence do not harden the material so much.   One may liken the effects of this carbide network to that of free cementite in ordinary tool steels ; the latter are distinctly harder when the cementite they possess exists as a network round the grains of pearlite than when it occurs as separate, more or less rounded, particles.
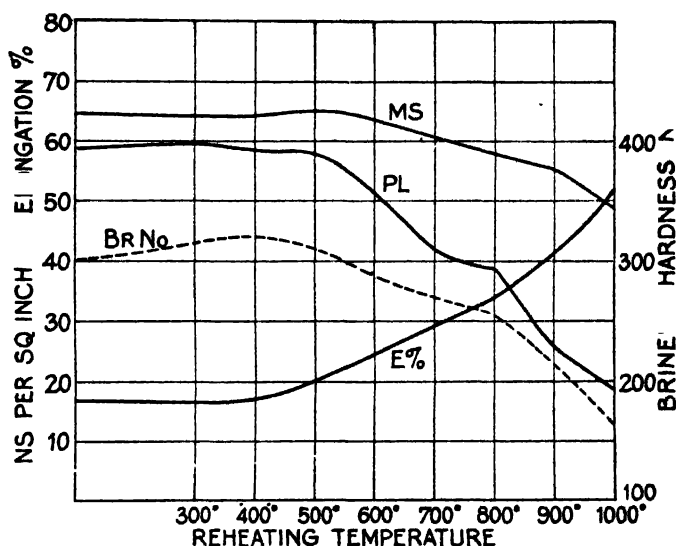
FIG. 117.   Effect of re-heating on tensile properties of cold-rolled strip.

Carbon	Chromium	Nickel
%	%	%
0·15	15·7	10·65

The results of tests on cold rolled "Anka" strip, after reheating to various temperature up to 1,000°C. are plotted in Fig. 117.   One may observe that the tensile strength falls fairly uniformily between 600° and 1000°C., but that the values for proof load* and Brinell hardness number show the characteristic break in the curve at 800°C.

Results on a rather less stably austenitic steel, containing 17·1 per cent. chromium and 8·1 per cent. nickel, are still

* The proof load is that producing an extension of 0·5 per cent. of the gauge length ; it is expressed in tons per square inch of the original cross-sectional area of the test piece.

more striking. As depicted in Fig. 118, the tensile strength rises slightly as the reheating temperature increases from 600° to 800°C., while the elongation values on the strips reheated in the range 500°/800°C. are all lower than that of the cold rolled strip. The curves for proof load and Brinell hardness number again exhibit the break at 800°C.
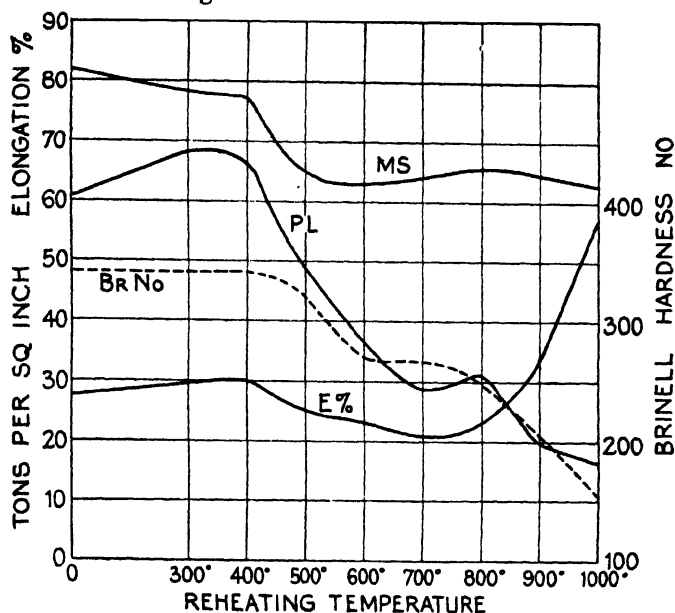
Fig. 118. Effect of re-heating on tensile properties of cold-rolled strip.

Carbon %	Chromium %	Nickel %
0·10	17 1	8·1

The lessened ductility referred to above may be ascribed to the presence of free carbide in the samples reheated to temperatures between 500° and 800°C. The same effect, in a rather more pronounced degree, may be noted in the results given in Table XLII, which relate to experiments on the cold rolled strip referred to in Fig. 118. Pieces of this strip were reheated to 850°/900°C., and slowly cooled; others were softened by reheating to 1,050°C., followed by cooling in the air. Some of each set of samples were then cold rolled, various amounts and the results of tests on these strips are collected in Table XLII. It is obvious that the strips which have been annealed at 850°/900°C. prior to the final

cold rolling are considerably less tough and ductile than those which had been softened at 1,050°C.

These results have an important bearing on the practical use of the steels for cold working operations and they will be referred to in a later chapter. Suffice it to say now that, although cold-worked austenitic steels may be partially softened by reheating to temperatures between 800° and 1,000°C., it is rare that practical use can be made of such partial softening. Generally speaking, when cold-worked material has to be softened, it should be reheated to temperatures between 1,000° and 1,200°C., depending on its composition, and not to any lower temperature.

TABLE XLII.

Effect of Annealing Temperature on Cold Rolled Strip.

Carbon	Chromium %	Nickel
0·10	17·1	8·1

Prior treatment : Cold Rolled 20 per cent.

Treatment.	Proof Stress.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 4 ins.	Reverse Bend over 3T.
Annealed 850°C.	31·8	59·6	20·0	
cold rolled 4%	44·9	62·5	15·0	
„ 10%	50·5	66·7	12·5	nil
A.C. 1050°C.	17·0	55·0	60·0	3
cold rolled 14%	38·5	73·2	36·0	1½
„ „ 19%	50·9	78·5	32·0	½

The microstructure of cold-worked material presents some interesting features. A slight amount of cold-work distorts the grains to some extent and also causes them to be crossed by series of fine parallel lines ; similar features are also often found in the microstructure of hot rolled bars. For example, Fig. 119 represents the structure of a rolled bar, one inch in diameter, of " Anka " steel ; rolling in this case commenced at about 1,100°C. and was completed by

about 900°C. When heavily cold-worked, the grain distortion becomes much more pronounced while the series of fine lines, becoming very numerous, produce a dark appearance in parts of the grains in the manner indicated in Fig. 120. When such cold-worked material is reheated, recrystallisation effects are very evident at 700°C., the heavily distorted grains visible in Fig. 120 being replaced by excessively fine equiaxed grains. Samples so treated, however, do not etch evenly ; thus the appearance of Fig. 121 suggests that recrystallisation has progressed further in the lighter portions than in the darker. As the reheating temperature rises, the fine dust-like grains just visible in Fig. 121 grow in size while the evidences of heterogeneity in structure become less pronounced. Fig. 122, for example, shows a sample after reheating to 900°C. Finally, in the case of this steel, all evidences of cold-work were removed at 1,000°C., producing the structure shown in Fig. 92 (page 168).

Reheating cold-worked material to temperatures between about 500° C. and 900° C., causes a precipitation of carbide, in addition to the more or less complete recrystallisation of the austenite ; but the mode of precipitation is not quite the same as in fully softened material similarly reheated. In the latter case, the carbide forms a network at the grain boundaries of the austenite but the grains themselves remain practically free from carbide, as is shown in Figs. 97 and 98. In cold-worked material, however, the carbide is precipitated not only along the grain boundaries, but also along the slip planes produced during the cold-working operation.

Probably the most striking characteristic of austenitic steel is that it cannot be hardened by quenching ; it is so contrary to the popular notion of steel being a carburised form of iron which may be so hardened. While the possession of this non-hardening capacity is in many ways an advantage, it has certain drawbacks. The property of hardening by quenching from suitable temperatures and that of lessening this induced hardness by tempering, permits one to harden locally—or to soften locally—with comparative ease, articles made from ordinary steel. For example, the cutting edges of chisels or of turning tools are hardened locally, the rest of the tool remaining soft. It is a more difficult operation to harden locally an article made from an austenitic steel, and it is well nigh impossible if the article already possesses its

Plate XXIV

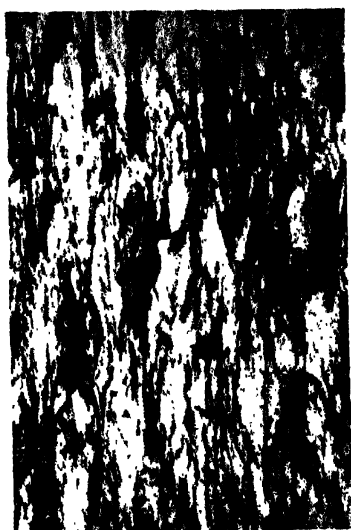FIG. 119. " Anka " steel, 0·10 % carbon, 15·2 % chromium and 11·4 % nickel, as rolled. × 750.

FIG. 120. ' Anka " steel, 0·10 % carbon, 15·2% chromium and 11·4 % nickel, cold-worked to a Brinell hardness number of 350. × 750

FIG. 121. Cold worked "Anka," as in Fig. 120, after re-heating at 700°C. × 750.

FIG. 122. Cold worked "Anka," as in Fig. 120, after re-heating at 900°C. × 750

[To face page 190.

final shape and dimensions.   There are certain purposes, however, where local hardness in an austenitic steel would be valuable.   For example, some of these steels have notable resistance to oxidation at high temperatures and on that account are used as valves for certain types of internal combustion engines where the head of the valve is quite likely to become red-hot during use.   The superior resistance to oxidation of these particular austenitic steels, and also their considerably greater strength at high temperatures, enable them to function more satisfactorily for such valves than ordinary steels and many other types of alloy steels. But the softness of the austenitic steel at ordinary temperatures, and also its low yield point, introduce a difficulty ; the tappet end of the stem of the valve, where it comes in contact with the tappet which operates it, becomes worn or mushroomed owing to the hammering action of the latter.   If the end of the stem could be hardened locally, the trouble would be avoided, but generally this is not feasible.   It has been suggested, however, that alloys containing less nickel than is necessary to make them completely austenitic would solve this difficulty.   Such alloys, as is evident from curves A and B, Fig. 85 and curve D, Fig. 87, may, by suitable treatment, be made either martensitic or austenitic ; hence in an article such as a valve, the head and most of the stem could be in the austenitic condition while the end of the stem could be made harder locally by suitable treatment and thus overcome the " mushrooming " difficulty mentioned above.   At first sight, the idea appears interesting—the head and the stem of the valve would be tough, a characteristic feature of these austenitic steels, while the foot would have the necessary hardness—until it is remembered that this austenitic head would also become hard after a brief sojourn in the range 600°/900°C. and hence very liable to break off.   The minimum temperature required to produce notable hardness in this manner would vary with the nickel and chromium contents of the steel, but curve D of Fig. 87 shows that it might occur at 550°/600°C. and valves which do not reach a higher temperature than 550°/600°C. in service can be made quite satisfactorily from much cheaper steels than these " borderland " austenitic-martensitic chromium-nickel steels.

Apart from this, however, the capacity for local hardening by heat treatment in such steels would be considered

dearly bought when the difficulties of working them are taken into account.   Thus when austenitic, they work-harden so rapidly that machining operations, particularly sawing and drilling, are difficult* and the same remark also applies, to many other manipulative processes, such as shearing and bending or straightening.   On the other hand, when hardened and tempered, they never become very soft as a reference to Figs. 85 and 86 shows.
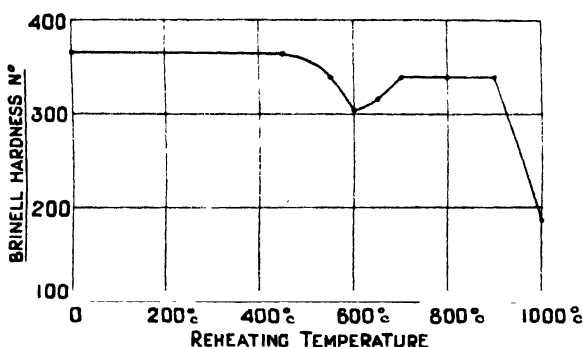
Fig. 123.

When a steel of this type is work-hardened and then reheated to successively higher temperatures, its hardness begins to fall at about 500°C., in the same way as the stably austenitic steels, and this continues up to about 600°C., but on heating to still higher temperatures, it hardens again owing to the production of martensite.   For example, Fig. 123, illustrates the behaviour of steel containing 0·16 per cent. carbon, 13·7 per cent. chromium and 7·85 per cent. nickel ; cylinders of this material were compressed twenty-four per cent. of their length and then reheated.   The curve in the diagram represents the Brinell hardness numbers of the several samples plotted against their respective reheating temperatures.   If this curve be compared with curve B in Fig. 85, where the Brinell hardness numbers ; obtained from the same steel after hardening at 850°/900°C. and then tempering are plotted, the striking similarity between the two curves will be apparent.

The expression " stably austenitic steel " has been used in the preceding pages to denote a steel which remained

* See page 508, re the machining of austenitic steels.

austenitic after reheating to any temperature, and curve C, in Fig. 82, was described as indicating the minimum nickel contents necessary to produce such steels. Further investigation, however, suggests that this statement is only true of steels containing this amount of nickel, if the word stable be used to mean " persistent " ; it is not correct if the word be given its physico-chemical meaning and understood to indicate equilibrium conditions. In the latter sense, the stable condition of alloys of the 18 : 8 type, for example, at temperatures below 400° C., is ferrite ; the austenitic form is only metastable at these temperatures. No amount of heating in this temperature range is likely, however, to bring about the change from metastable to stable form. The persistence of the austenitic form below 400° C. is due to the extreme sluggishness of high chromium alloys to undergo any structural change except at quite high temperatures. Once these alloys have been made austenitic, by heating to 1,000° C. or over, they remain so even after the slowest possible rate of cooling or after holding for very long periods at temperatures of 400° C. or lower. From the point of view of persistence in structure at any temperature, it may be said definitely that those alloys whose compositions lie above curve C, in Fig. 82, are austenitic and, barring the precipitation of carbide described in the preceding pages, they remain so after any form of heat treatment.

If, however these alloys are cold-worked, they become magnetic to a greater or less extent, indicating that at least a partial change from austenite to ferrite has taken place in the steel. It may be supposed that the distortion produced by cold-work supplies the necessary agitation to the austenitic crystal structure to enable it to revert, in part at least, to equilibrium conditions. As would be expected, therefore, the production of magnetism is especially marked when " borderland " alloys, such as that to which Fig. 123 refers, are cold-worked ; these are austenitic only when quenched from high temperatures and their stability in this condition is easily upset. Magnetic effects are, however, quite evident in steels whose nickel content is as high as is indicated by curve C, Fig. 82, but they diminish as the content of this metal is raised still higher.

Definite evidence of the change from austenite to ferrite as a result of cold-work on a steel containing about

18 per cent. chromium and 8 per cent. nickel, was obtained by Dr. Westgren,* who submitted to X-ray examination samples of Staybrite steel before and after cold-working. The X-ray photograms showed conclusively that the original face-centred lattice structure of the γ-iron (austenite) in the soft material had been changed in part by cold-working into the body-centred lattice characteristic of a-iron.

A detailed investigation of the effect of cold-work on alloys of the 18 : 8 type was carried out by Bain and Aborn,† who made use of X-ray and magnetic permeability measurements. As a result of extremely severe cold-work at low temperatures, it was found possible to produce an alloy of this type in which over 90 per cent. of the austenite had been transformed to ferrite. Such a condition would have no practical application as the alloys develop cold-work cracks long before they reach this stage. Experiments on such severely cold-worked samples, before and after re-heating to various temperatures, enabled Bain and Aborn to show that ferrite was the stable phase below about 400° C., and austenite above about 600° C. Between these two temperatures, mixtures of ferrite and austenite existed. As a result of these and other experiments, Bain and Aborn concluded that equilibrium conditions for alloys containing, on the one hand, 18 per cent. chromium and variable nickel and, on the other hand, 8 per cent. nickel and variable chromium, were approximately as indicated in Fig. 124. It should be reiterated that the conditions set out in these diagrams are those of theoretical stability ; although they may be produced, in part at least, by severe cold-work, they do not represent the conditions obtained by any form of heat treatment.

These results and diagrams are exceedingly interesting, however, and they have an important bearing on the use of the steel at temperatures between 400° C. and 600° C. Reference to Fig. 116 shows that cold-worked alloys of the 18 : 8 type, are not appreciably softened by reheating for half-an-hour at 500° C. If the data obtained by Bain and Aborn be correct, recrystallisation of the cold-worked ferrite commences at about 400° C. ; at about 600° C. it is replaced by austenite.

* See " Chromium Nickel Rustless Steel," Dr. W. H. Hatfield, " The Metallurgist " (Supplement to the " Engineer "), October 30th, 1925.

† *Loc. cit.*

Such changes, however, take place very slowly ; for example, in one experiment at 600° C., equilibrium was not obtained in less than 250/300 hours. It is to be expected that much longer periods would be required, e.g., at 500° C., but presumably a considerable degree of recrystallisation would eventually be produced at this temperature. It is difficult to conceive how such a recrystallisation could occur without
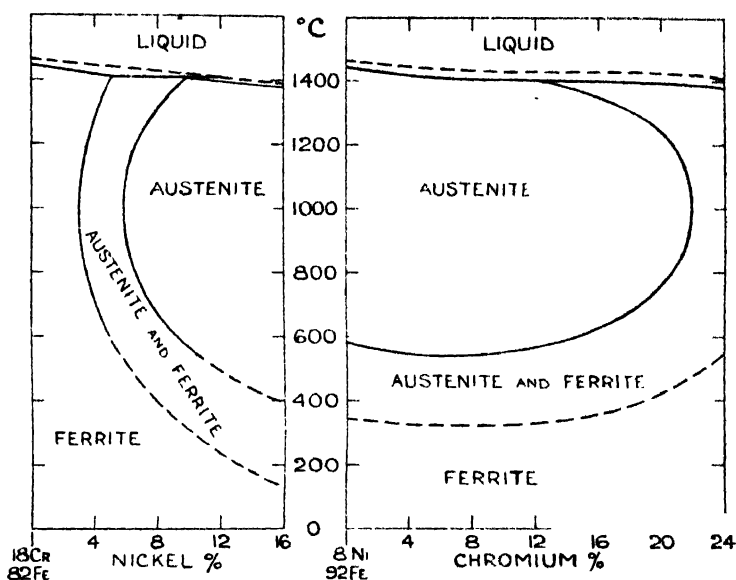
FIG. 124. Diagram showing the approximate constitution (under equilibrium conditions) of the 18 per cent. chromium alloys with variable nickel and the 8 per cent. nickel alloys with variable chromium.

part of the hardness induced by cold-work being concurrently removed ; it seems likely, therefore, that the prolonged heating of these cold-worked alloys at temperatures in the range of 400°/500° C., will cause them to soften to some extent. Further, it may be presumed from the left hand part of Fig. 124, that a distinctly higher nickel content than 8 per cent. will increase the stability of the austenite during cold-working operations. Such alloys undoubtedly work harder at a slower rate than those containing 8 per cent. nickel or thereabouts.

(6) Effects of Other Alloys on the "Anka" "Staybrite" "V.2.A." Steels.

The austenitic chromium-nickel steels of the "Anka"-"Staybrite-V.2.A." type withstand the corrosive attack of a much wider range of chemicals than do the straight chromium steels, but they are by no means immune from the attack of all chemicals; hence various efforts have been made to extend their usefulness by adding to them other metals such as silicon, molybdenum, tungsten, copper, and aluminium, most of the complex alloys thus produced being the subject of patents. Among the earliest efforts in this direction were those of Dr. Strauss, as a result of which, Messrs. F. Krupp, A.G., took out patents* in 1922 for the addition of copper and molybdenum respectively. In the former case the composition specified was 18/24 per cent. chromium, 7/20 per cent. nickel, 2/6 per cent. copper and 0·1/0·4 per cent. carbon, the particular property claimed being resistance to ammonium chloride. The addition of molybdenum was stated to increase greatly the resistance of the steel to the action of sulphurous acid at high pressures and temperatures, such as occur in the manufacture of cellulose; the range of composition claimed was 18/30 per cent. chromium, 4/20 per cent. nickel, 2/4 per cent. molybdenum and 0·1/0·4 per cent. carbon. These two steels were put on the market as "V.6.A." and "V.4.A." respectively and they may obviously be regarded as modifications of "V.2.A." Somewhat similar steels have been produced by Messrs. Brown, Bayley's Steel Works, Ltd., under the names "Anka II" or "BB4K" and "Anka III."

In the same year, C. M. Johnson took out patents† in the United States of America for chromium-nickel steels to which silicon was added. In the earlier patent, the material was to contain 10/20 per cent. chromium, 9/25 per cent. nickel and 1/10 per cent. silicon. The second patent called for a higher percentage of nickel, at least double the chromium content, but a similar range of silicon was specified. A series of alloys, known under the general term "Rezistal" have been made by the Crucible Steel Co. of America in accordance with these patents. In 1923, Sir R. A. Hadfield

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* German patents 395,044 and 399,806 (August 3rd, 1922). British patents 201,914 and 201,915 (July 31st, 1923).

† U.S. patents 1,420,707 and 1,420,708 (June 27th, 1922).

patented an alloy containing 8/25 per cent. chromium, 5/17 per cent. nickel, 0·4/8·0 per cent. manganese and 0·7/10·0 per cent. silicon to which 1/10 per cent. tungsten or an equivalent amount of molybdenum could be added.* The carbon content was to be not more than 1 per cent. ‡ small percentages of cobalt, vanadium, titanium or aluminium could also be added and great resistance to oxidation at high temperatures and to attack by hot vapours and gases was claimed, together with strength and toughness at high temperatures.

The following year a further United States patent† was granted to P. A. E. Armstrong and R. P. de Vries for an alloy containing 0·05/0·5 per cent. carbon, 5/25 per cent. chromium, 4/30 per cent. nickel and 1·5/6·0 per cent. silicon, which was described as a tough, stable surface alloy.

In 1926, a further patent‡ on the addition of copper was obtained by Messrs. Edgar Allen & Co. (Sheffield). These patentees stated that the copper content should be less than 2·0 per cent. (which, it may be noted, is the lower limit of the Krupp patent) and preferably not more than 1·5 per cent. while the selected proportions of chromium, nickel and carbon were respectively 7/20 per cent., 4/20 per cent. and 0·05/0·5 per cent.

In 1928, N. V. Hybinette§ claimed an alloy containing 15/25 per cent. chromium, 5/10 per cent. nickel, 1/2 per cent. carbon and 0·5/2·0 per cent. aluminium as being particularly resistant to heat.

It is difficult to say to what extent these various alloys have actually been used commercially and, so far as the author can gather, very little information has been published as to the physical properties of some of them. Generally speaking, the addition of other metals to a chromium-nickel steel, which is very stably austenitic, raises its tensile strength and hardness somewhat, though copper appears to be an exception in this respect. With regard to carbon content, if the modified alloys are intended to be rolled or forged into various shapes and then fabricated into plant, the amount of this element should be kept low,

* British patent 232,656 (December 27th, 1923).

† U.S. patent 1,513,793 (November 4th, 1924).

‡ English patent 267,024 (September 28th, 1926).

§ U.S. patent 1,675,709 (July 3rd, 1928).

e.g., about 0·1 per cent.   A greater amount hardens the alloys, in some cases very appreciably, and this may be useful if strength at high temperatures is a desirable property.   The results in Table **XLIII** indicate the type of mechanical properties which may be expected from these complex alloys.

It will be noticed that several of them, even when of low carbon content, require reheating to high temperatures before they acquire the characteristic toughness of austenitic steels ; some of the higher carbon steels, indeed, do not attain this toughness even when quenched from 1,200°C.   These characteristics seem to be due to the fact that the carbide in such steels requires a much higher temperature for its complete solution than in the parent chromium-nickel steels ; in most of these complex alloys (even if containing only 0·1/0·15 per cent carbon) notable amounts of carbide are visible in the structure of samples quenched from 1,000°C.

Again, the presence of considerable quantities of either silicon, molybdenum or tungsten—all of which behave like chromium in lessening the range of existence of γ-iron (see page 68)—frequently causes the resulting alloy to be duplex in structure.   When quenched from high temperatures such alloys consist of mixtures of austenite and ferrite.   For

TABLE XLIII.

Mechanical Properties of Complex Austenitic Steels.

No.	Carbon %	Chromium %	Nickel %	Silicon %	Copper %	Molybdenum %	Tungsten %
(1)	0·10	17·8	10·1	0·36	2·20	—	—
(2)	0·26	17·4	10·8	0·49	2·45	—	—
(3)	0·15	15·6	10·0	1·43	—	—	—
(4)	0·10	15·4	10·3	3·28	—	—	—
(5)	0·11	14·9	10·2	4·59	—	—	—
(6)	0·12	16·4	10·0	0·31	—	—	1·03
(7)	0·17	15·5	11·0	0·40	—	—	2·00
(8)	0·24	15·5	11·5	0·36	—	—	3·65
(9)	0·22	16·1	10·9	1·95	—	—	3·80
(10)	0·15	18·1	9·3	0·74	—	—	0·74
(11)	0·13	17·5	8·5	0·28	—	—	1·05
(12)	0·17	22·2	10·0	0·44	—	—	1·83
(13)	0·12	17·2	10·5	0·70	—	2·64	—
(14)	0·13	17·2	10·1	0·54	—	3·42	—
(15)	0·16	20·1	7·1	0·45	—	4·2	—
(16)	0·14	19·9	10·1	0·51	—	4·1	—
(17)	0·34	20·8	8·4	0·62	—	3·6	—
(18)	0·37	12·5	12·8	1·86	—	—	2·34
(19)	0·45	12·7	12·8	1·75	—	—	2·1
(20)	0·29	17·7	9·3	0·48	—	—	1·64
(21)	0·38	18·7	9·7	1·21	—	—	3·27
(22)	0·30	17·7	7·0	1·46	—	—	4·23

Plate XXV

Fig. 125. Steel containing 0·16% carbon, 20·1% chromium, 7·1% nickel, 4·2 molybdenum. W.Q. 1150°/1200° C. × 200 (austenite and ferrite).

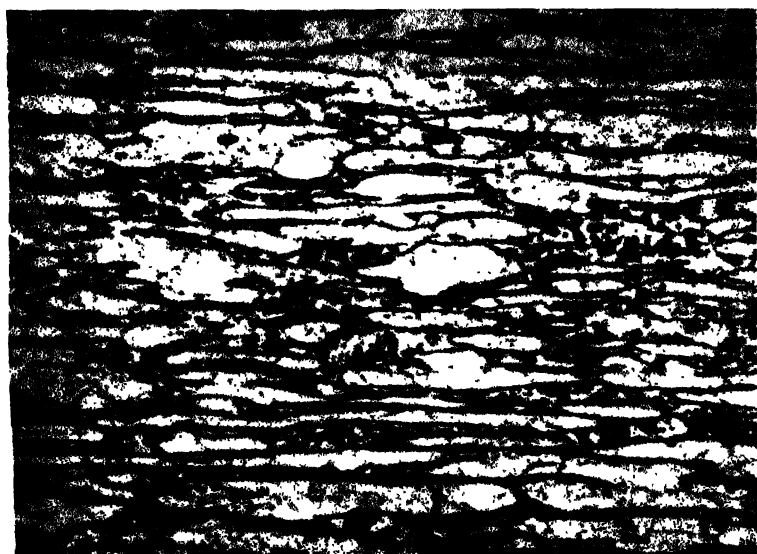Fig. 126 Steel containing 0·16% carbon, 20·1% chromium, 7·1% nickel, 4·2% molybdenum. W.Q. 1000°C. × 200 (austenite, ferrite and carbide).

TABLE XLIII—*Continued*.

No.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent on 2 ins.	Reduction of Area per cent.	Brinell Hardness No.	Izod Impact, ft. lbs.
(1)	W.Q. 1000°C.	16·4	34·0	67·0	77·1	131	103
	W.Q. 1100°C.	15·4	33·2	66·0	77·9	126	100
(2)	W.Q. 1000°C.	33·0	47·2	37·0	51·0	196	65
	W.Q. 1100°C.	23·0	45·0	49·0	59·3	179	96
(3)	W.Q. 1000°C.	23·2	48·3	60·0	70·7	207	118
	W.Q. 1100°C.	21·0	45·4	70·0	76·2	170	120
(4	W.Q. 1000°C.	32·8	57·5	47·5	61·5	223	117
	W.Q. 1100°C.	20·8	49·6	62·0	71·7	196	120
(5)	W.Q. 1000°C.	37·2	72·2	47·0	53·4	228	104
	W.Q. 1100°C.	31·4	69·0	61·0	61·5	228	120
(6)	W.Q. 1000°C.	19·4	41·4	66·5	71·7	149	107
	W.Q. 1100°C.	19·5	42·0	69·5	70·7	149	105
(7)	W.Q. 1000°C.	25·6	44·4	48·0	60·4	170	106
	W.Q. 1100°C.	25·2	42·0	58·5	65·8	156	120
(8)	W.Q. 1000°C.	39·2	48·0	41·0	52·2	217	78
	W.Q. 1100°C.	25·4	45·2	56·0	57·0	187	101
(9)	W.Q. 1000°C.	32·0	50·0	50·0	59·3	217	78
	W.Q. 1100°C.	28·4	49·0	61·0	64·8	196	109
(10)	W.Q. 1000°C.	16·8	43·2	71·0	77·0	163	118
	W.Q. 1100°C.	16·9	42·9	73·5	77·9	149	120
(11)	W.Q. 1000°C.	21·7	48·6	61·0	59·2	179	120
	W.Q. 1100°C.	18·4	44·6	73·0	67·8	156	120
(12)	W.Q. 1000°C.	24·0	42·4	58·0	62·2	187	90
	W.Q. 1100°C.	22·4	40·3	52·0	66·8	187	107
(13)	W.Q. 1000°C.	24·0	43·2	60·8	66·8	179	101
	W.Q. 1100°C.	16·0	40·8	74·0	73·4	131	—
(14)	W.Q. 1000°C.	22·0	48·0	56·0	67·8	183	104
	W.Q. 1100°C.	19·2	45·0	69·5	73·6	159	109
(15))	W.Q. 1000°C.	30·0	50·0	33·0	45·2	241	26
	W.Q. 1150°C.	33·5	46·1	46·0	62·0	223	118
(16)	W.Q. 1000°C.	35·6	47·4	30·0	37·8	228	21
	W.Q. 1150°C.	32·4	44·4	51·0	67·8	196	120
(17)	W.Q. 1000°C.	34·0	54·6	34·5	44·6	248	34
	W.Q. 1150°C.	30·0	53·7	44·5	53·4	228	52
(18)	W.Q. 1000°C.	36·0	55·8	39·0	53·4	241	78
(19)	A.C. 800°C.	42·0	68·0	27·0	45·0	269	55
(20)	W.Q. 1000°C.	31·0	51·2	42·0	52·0	217	
	W.Q. 1100°C.	29·4	46·6	57·0	63·7	179	
	W.Q. 1200°C.	24·0	45·6	66·5	69·8	179	
(21)	A.C. 1000°C.	29·2	50·6	27·5	28·9		
(22)	A.C. 1000°C.	38·0	58·5	37·5	52·0		

example, Fig. 125 represents the structure of a steel containing about 4 per cent. molybdenum after quenching from 1,150°C.; the two constituents are austenite (light) and ferrite. When quenched from 1,000°C., there was rather less ferrite, but a considerable amount of carbide was also present, see Fig. 126.

When cold-worked, these complex alloys behave, in the main, in a similar manner to the chromium-nickel alloys previously described; they harden rapidly but the actual

rate depends on their composition.   The results of some tests are given in Fig. 127.   Obviously for operations involving extensive cold deformation, one would choose as soft an alloy as possible ; for example, a material such as that to which curve B relates would be much more amenable in this respect than the one whose characteristics are plotted in curve E.
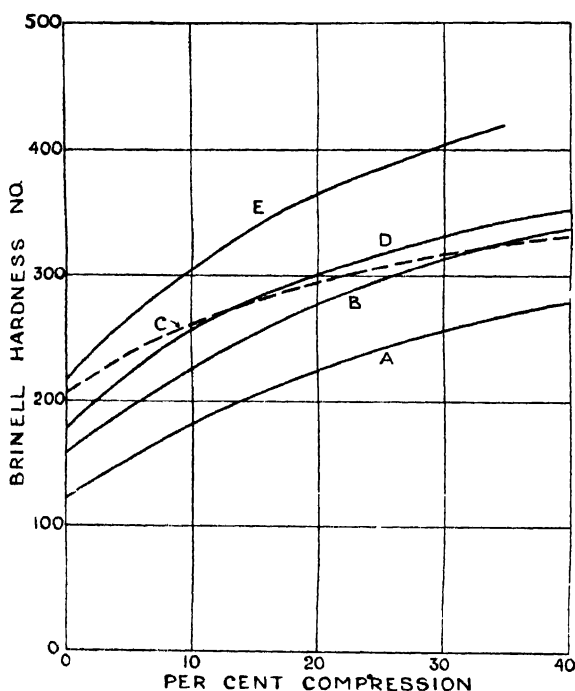

Fig. 127. Work hardening tests on complex austenitic alloys.

Curve	Carbon %	Chromium	Nickel %	Copper %	Molybdenum %	Tungsten %	Treatment
A	0·10	17·8	10·1	2·2	—		W.Q. 1,000° C.
B	0·13	17·2	10·1	—	3·42		W.Q. 1,100° C.
C	0·16	20·1	7·1	—	4·2		W.Q. 1,150° C.
D	0·29	17·7	9·7	—	—	1·64	W.Q. 1,000° C.
E	0·39	19·0	7·0	—	3·65		W.Q. 1,100° C.

Complex alloys similar to those described in Table XLIII behave in much the same manner, on reheating, as do the simpler chromium-nickel alloys.   If previously work-hardened, they are fully softened by reheating in the range 1,000°/1,200°C. ;   and in cases where the alloy contains molybdenum, silicon or tungsten and the carbon content

is much above 0·1 per cent, the required temperature will be nearer 1,200°C than 1,000°C. Thus Messrs. F. Krupp recommend 1,200°C. for softening their "V.4.A." brand and Fig. 128 shows the Brinell results obtained on re-heating a rolled bar of a tungsten bearing steel ;* the latter steel still contained some free carbide after quenching from 1,200°C.
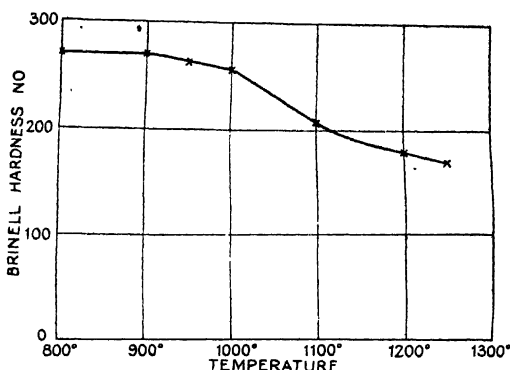

FIG. 128.   Relation between reheating temperature and hardness of rolled bar.

Carbon	Silicon	Chromium	Nickel	Tungsten
0·45%	1·75%	12·67%	12·81%	2·1%

At lower temperatures, in the range 500°/900°C., or thereabouts, precipitation of carbide takes place in a similar manner to the simpler chromium-nickel austenitic steels. It is probable that the rate of precipitation is appreciably affected by the added alloy ; some of the complex alloys are undoubtedly more stable, structurally, than the "Anka-Staybrite-V.2.A." type of alloy, at these low temperatures, but it is doubtful whether any of the steels are entirely free from this very troublesome defect.

(7)   CHROMIUM-NICKEL STEELS WITH A HIGH CHROMIUM OR NICKEL CONTENT.

From a commercial point of view, the "Anka-Staybrite-V.2.A." type of steel is undoubtedly the most important of the austenitic chromium-nickel rustless steels, especially if importance be measured in terms of tonnage produced ;

* See "Valve Steels." P. B. Henshaw. J.R.Ae.Soc., March, 1927.

but there are more highly alloyed types, which have a limited application for special purposes.

The range of composition specified in the earlier Krupp patents extends to 40 per cent. chromium and 20 per cent. nickel and although the author is not aware of the commercial use of alloys with so high a chromium content as 40 per cent., the " N.C.T.3." alloy made by the Essen firm contains about 25 per cent. chromium and 20 per cent. nickel. This alloy has been developed for its heat resisting properties, for which purpose its use was patented in 1926 in Germany and 1927 in this country.* The range of composition specified in the patent is 15/25 per cent. chromium and a like amount of nickel but an equally important feature appears to be in regard to carbon, the content of which is limited to less than 0·2 per cent. Special emphasis is laid on this in the patent, a higher carbon content being alleged to reduce considerably resistance to oxidation. Thus it is stated : " An alloy with 15 per cent. chromium and 25 per cent. nickel resists oxidation up to 1,150°C. when containing 0·45 per cent. carbon and up to 1,300°C. when containing under other equal conditions, 0·1 per cent. carbon."

The properties of alloys containing more than about 25 per cent. chromium possess several interesting features. If reference be made to Fig. 82, it will be noted that the amount of nickel required to produce an austenitic steel falls as the chromium content rises up to about 20 per cent. In the light of what has been said as to the influence of chromium on the gamma range of iron and the structure of high chromium irons, it is obvious that this substitution of nickel by chromium cannot continue indefinitely, particularly if the carbon content be reduced to a low value. On the contrary, as the presence of more than about 15 per cent. chromium eliminates the gamma range from pure iron, it would be expected that more nickel rather than less would be required to produce a stably austenitic condition in low carbon alloys containing considerably more than this amount of chromium. This is actually found to be the case. According to E. C. Bain and W. E. Griffiths,† the stably austenitic condition is only found in low carbon alloys containing more

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* British patent 276,317 (July 25th, 1927).

† " An Introduction to the Iron-Chromium-Nickel Alloys." *Trans. Amer. Inst. Min. & Met. Eng.*, 1927, Vol. 75, p. 166.

nickel than is indicated by the line ABC in Fig. 129.   It will be observed that the requisite content of this metal falls to a minimum at about 20 per cent. chromium and rises sharply when the amount of the latter metal exceeds 25 per cent. As noted earlier, Bain and Griffiths place the minimum nickel content for steels containing up to 20 per cent. chromium at a distinctly higher figure than Strauss and Maurer, see Fig. 82 (page 144). The difference is due in some degree to carbon content, the steels used by Bain and Griffiths containing less than those of Strauss and Maurer (and, as has been shown earlier, the presence of carbon increases the austenitic range in high chromium steels), but probably in much greater measure to differences in treatment.   Fig. 129 (and curve C in Fig. 82) is founded on the results obtained by the examination of samples which had been drastically annealed.   The results obtained by Strauss and Maurer on the other hand, relate to samples which, while not necessarily quenched in water from high temperatures, had been cooled at a relatively rapid rate compared to the exceedingly slow annealing used by Bain and Griffiths.
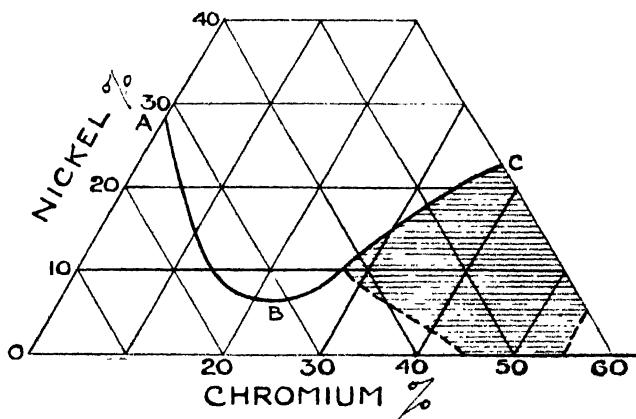

Fig. 129.   Constitution of iron-chromium-nickel alloys (Bain and Griffiths).

The cross hatched area in Fig. 129 indicates the approximate range of composition in which Bain and Griffiths found the " brittle constituent " (see page 80) to be produced to a greater or less extent on drastic annealing.   Such alloys would obviously be unsuitable to use, for example, for heat

resisting purposes involving prolonged exposure to the range of temperature which gives rise to this peculiar brittle form of the material.   The use of alloys containing so large an amount of chromium is still in the experimental stage and it would appear that a better understanding of their properties and peculiarities is desirable before their commercial use can be recommended.

Material with a still higher nickel, but lower chromium, content was patented by the Sociétè Anonyme de Commentry, Fourchambault et Decaseville and is produced by this firm under the name " A.T.V."   There are a number of patents but they may be divided into three groups :—

(1) Nos. 140,507 (Dec. 17, 1918) and 159,492 (Nov. 11, 1920) ; alloys containing 0·2/1·0 per cent. carbon, 10/15 per cent. chromium, 20/25 per cent. nickel and 1/5 per cent. manganese, to which may be added 0·2/1·0 per cent. vanadium, 0·1/0·5 per cent. titanium, 0·5/5·0 per cent. tungsten, 0·2/3·0 per cent. molybdenum and up to 10 per cent. cobalt.   Resistance to shock or high pressure and to the action of strong acids, organic acids and alkalies is claimed.

(2) Nos. 140,509 (Dec. 17, 1918) and 159,858 (Nov. 5, 1920); alloys containing 0·3/1·0 per cent. carbon, 8/15 per cent. chromium, 25/40 per cent. nickel and 1/5 per cent. manganese, to which may be added tungsten or molybdenum to the extent of 0·2/5·0 per cent.   This alloy is claimed to be resistant to superheated vapours and to hot and moist gases, to have good wearing qualities and a co-efficient of expansion which may be varied between 0·000008 and 0·00017 per degree centigrade.

(3) Nos. 140,508 (Dec. 17, 1918) and 159,857 (Nov. 5, 1920) ; alloys containing 0·3/1·0 per cent. carbon, 8/25 per cent. chromium, 50/80 per cent. nickel, 1/5 per cent. manganese and 0·5/8·0 per cent. tungsten ; the latter metal may be wholly or partially replaced by 0·2/5·0 per cent. molybdenum, and titanium, vanadium or cobalt may be added in the proportions of 0·1/0·2 per cent., 0·2/1·0 per cent. and up to 10 per cent. respectively. This alloy is stated to possess high mechanical strength at high temperatures and to be resistant to the action of chemicals.

In the above list, the numbers and dates of the British patents are given, but patents were also taken out in other countries. It may be mentioned that the British rights for these patents are held by Messrs. Hadfields, Ltd. The range of composition specified is very wide and it is very probable that a number of types of alloys are made by the French firm and their British confrères. Some samples which came under the author's notice, had the following compositions :—

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Tungsten %
0·41	0·19	0·75	11·1	38·4	nil
0·44	0·13	1·56	13·5	27·9	3·7
0·46	1·20	1·09	14·0	26·5	3·6
0·42	1·50	1·21	14·3	27·9	3·5
0·29	1·41	0·98	13·1	26·4	2·2
0·45	1·49	0·90	13·6	25·9	3·0
0·43	0·25	—	10·4	36·3	nil

The patents obtained by C. M. Johnson, which were referred to on page 27 also include steels which come in the high nickel category. These patents are owned by the Crucible Steel Company of America and several varieties of steels, collectively termed "Rezistal," are made by this firm. Two of these types of steels have approximately the following analyses :—

Mark.	Carbon %	Silicon %	Chromium %	Nickel %
No. 4 ...	0·2 max.	2·5/3·0	16/18	24/26
No. 7 ...	0·25 max.	1·5/2·0	24/26	20/22

Silicon, it will be noted, is an essential constituent.

Since 1922, the date of the Johnson patents, a number of patents have been obtained in different countries by various firms. The brief account given in Table XLIV is not claimed to be complete but it indicates the trend of modern developments and the extreme complexity of the patent situation ; the most remarkable thing from a layman's point of view is the way in which the various patents appear to overlap and even to duplicate each other.

<center>TABLE XLIV.</center>

<center>*Patents relating to high nickel alloys.*</center>

<center>*(1923 and onwards).*</center>

Patent.	Date.	Particulars.
E.P. 220,710	5/7/23	H. Etchells, A. Popplewell and L. Cameron & Son, Ltd. Alloy containing 5/30 per cent. chromium, 26/50 per cent. nickel, 25/69 per cent. iron and not more than 0·25 per cent. carbon. Nickel replaceable wholly or in part by cobalt. Not corroded by acids, alkalies or salts and suitable for decorative articles, table-ware, cooking utensils and parts exposed to sea water.
U.S.P. 1,496,505	3/6/24	H. F. Whittaker and T. Baker. Iron or steel alloyed with about 40 per cent. nickel and up to 10 per cent. chromium has co-efficient of expansion equal to that of resistant glass and enamel and is suitable for the manufacture of glass—or enamel—lined metal vessels.
E.P. 221,511	5/9/24	Poldihutte. Stainless steel alloy particularly resistant to hydrochloric or sulphuric acids contains 9/27 per cent. chromium, 20/25 per cent. nickel, not more than 0·35 per cent. carbon and not more than 0·5 per cent. each silicon and manganese.
E.P. 236,931	1/7/25	N. V. Hybinette. Alloys particularly resistant to the action of alkalies contain 28/40 per cent. chromium, 18/40 per cent. nickel; may also contain up to 10 per cent. cobalt or 2 per cent. copper. Preferred composition contains 30 per cent. chromium, 20 or 35 per cent. nickel, 1·5 per cent. carbon, 1·0 per cent. silicon and 0·5 per cent. each aluminium and manganese.

TABLE XLIV—*Continued.*

Patent.	Date.	Particulars.
U.S.P. 1,568,578	1/12/25	N. V. Hybinette. Heat resisting alloys contain 10/20 per cent. chromium, 30/40 per cent. nickel, 0·4/1·5 per cent. carbon, and less than 1·0 per cent. silicon.
E.P. 286,367	3/12/26	Heraeus Vacuumschmelze, A.G. Alloys for turbine blades and machine parts exposed to similar conditions contain 10/40 per cent. chromium, 40/85 per cent. nickel, 1/40 per cent. iron and practically no carbon. 0/15 per cent. tungsten, 0/12 per cent. molybdenum, 0/6 per cent. aluminium and 2/20 per cent. cobalt may be present.
U.S.P. 1,617,334	15/2/27	C. M. Johnson. A steel containing 25/30 per cent. chromium, 20/30 per cent. nickel and 1/3·5 per cent. silicon.
E.P. 276,249	26/2/27	Cammell Laird & Co., Ltd. Alloys possessing strength and resistance to scaling at high temperatures and not liable to crack or warp on cooling, contain 16/22 per cent. chromium, 26/30 per cent. nickel, 0·85/0·55 per cent. carbon and 0·8/0·5 per cent. each silicon and manganese. They are suitable for case hardening retorts, annealing boxes, furnace grates and fire bars.

The third group of the "A.T.V." patents really passes into the range of the "nichromes," that group of heat resisting alloys which have come so widely into use largely as a result of the rapid development of electrical resistance methods of heating, and which generally contain 50/80 per cent. nickel, 10/30 per cent. chromium and up to about 25 per cent. iron, with smaller amounts of carbon, silicon and manganese. The general relationship between these alloys and the "stainless steels" discussed up to now is indicated broadly on the ternary iron-nickel-chromium diagram reproduced in Fig. 180. The shaded part near the iron corner

of the diagram includes the ranges of composition covered by the Krupp " A.T.V." (groups 1 and 2 only), Johnson and Cameron patents. The dotted curve indicates the area*
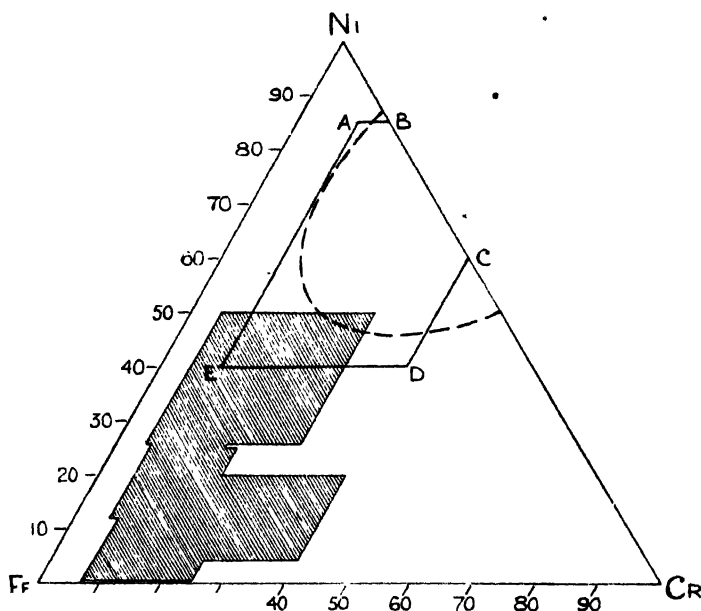

FIG. 130. Ranges of composition of corrosion resisting alloys.

in which most of the commercial alloys of the " nichrome " type fall, while the area ABCDE covers the range of composition of practically carbonless alloys claimed by Heraeus Vacuumschmelze A.G. for use as turbine blading or as machine parts exposed to similar conditions.† Broadly speaking, it may be said that all'alloys containing between 8 or 10 per cent. and 40 per cent. chromium, and the remainder iron and nickel in any proportions, are the subjects of patents as material resistant to corrosion in some form or another.

Chromium-nickel steels containing 20 per cent. nickel or more are relatively expensive; also, unless their carbon content is very low, they are difficult to forge or roll or

* See " Heat and Acid Resisting Alloys (Ni-Cr-Fe)," J. F. Kayser. *Trans. Faraday Soc.*, Vol. XIX, 184.

† British patent 286,367 (December 3rd, 1926); see Table XLIV.

otherwise hot work owing to the fact that they retain at
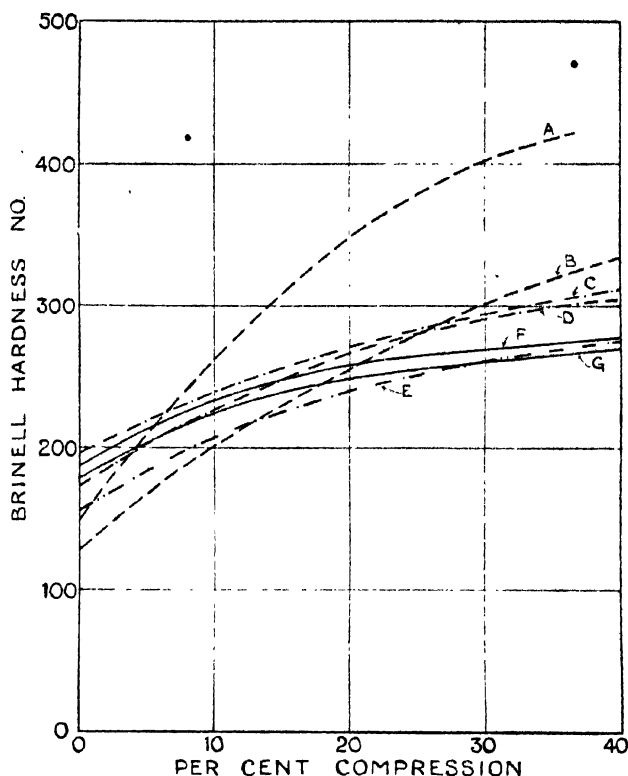high temperatures a greater proportion of their strength than

FIG. 131.   Work hardening tests : high nickel alloys.

Curve	Carbon %	Silicon %	Chromium	Nickel %	Tungsten %
A	0·12	0·30	18·0	8·2	
B	0·09	0·17	16·0	10·6	
C	0·29	2·68	17·1	25· 3	
D	0·13	2·65	17·1	25·4	
E	0·16	0·23	11·7	23·9	
F	0·33	0·33	11·6	35·5	3·5
G	0·32	0·46	11·4	35·3	

do the less alloyed steels.   This latter property is, of course, of
very considerable value for certain engineering purposes, but

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it increases the cost of working the alloys and also limits the forms, apart from castings, in which they may be produced commercially to those of simple section, such as round or rectangular bars.   The hot rolling of special sections, for example, those for turbine blading, is attended with great difficulty so that several of the alloys may only be produced commercially in such special sections by machining from round or rectangular bars, a very expensive and wasteful method.   Similarly, the production of weldless tube is not yet possible with many of them.   It is likely, therefore, that these rich alloys will only be used commercially where the less alloyed and cheaper steels definitely fail to give satisfactory service.

Table XLV gives data regarding the mechanical properties of some of these materials containing high nickel or chromium or both.   Fig. 131 shows that when cold-worked, the high nickel alloys harden at a rather slower rate than the ordinary " Anka-Staybrite-V.2.A." type of alloy. The ease of cold-working, however, depends on the initial hardness and this may be considerably higher than in the steels of lower nickel content.

TABLE XLV.

Mechanical Properties of Alloys with High Nickel or Chromium Content.

No.	Carbon %	Silicon %	Chromium %	Nickel %	Tungsten %
(1)	0·16	0·23	11·7	23·9	nil
(2)	0·13	0·44	11·5	35·4	,,
(3)	0·32	0·46	11·4	35·3	,,
(4)	0·14	0·30	11·8	35·6	3·40
(5)	0·33	0·33	11·6	35·5	3·50
(6)	0·35	1·36	10·9	35·2	nil
(7)	0·44	0·93	16·0	31·9	,,
(8)	0·46	1·20	14·0	26·5	3·59
(9)	0·13	2·65	17·1	25·4	nil
(10)	0·29	2·68	17·1	25·3	,,
(11)	0·13	2·68	17·0	25·2	3·30
(12)	0·32	2·76	17·0	25·1	3·50
(13)	0·33	1·22	16·9	24·3	nil
(14)	0·10	0·91	25·1	20·9	,,
(15)	0·19	0·80	20·3	19·3	,,
(16)	0·29	1·81	14·9	24·8	2·86
(17)	0·52	1·41	23·9	22·3	3·13

TABLE XLV—*Continued.*

No.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 6 ins.	Reduction of Area per cent.	Brinell Hardness No.	Izod Impact, ft. lbs.		
(1)	W.Q. 1000°C.	18·2	39·8	45·0	65·8	156	102	116	107
(2)		16·4	36·6	44·0	65·8	149	115	115	114
	W.Q. 1150°C. ...	10·4	35·5	50·0	71·7	151	109	109	110
(3)	W.Q. 1000°C. ...	18·0	39·6	38·0	58·2	156	84	86	80
	W.Q. 1150°C. ...	18·0	40·4	40·0	59·3	163	87	95	95
(4)	W.Q. 1000°C. ...	22·0	44·6	31·0	57·0	183	93	116	95
	W.Q. 1150°C. ...	18·6	40·9	44·0	66·8	156	110	120	120
(5)	W.Q. 1000°C. ...	26·0	46·1	27·5	44·6	187	55	55	55
	W.Q. 1150°C. ...	18·9	44·4	33·0	54·3	179	72	70	78
(6)	Rolled	24·0	46·0	31·0	51·0	—	—		
(7)	Rolled	35·0	47·6	26·0	39·2	207	17	25	25
	W.Q. 1000°C. ...	24·0	45·6	32·5	44·6	187	29	29	27
(8)	Rolled	—	45·9	34·5	42·5	—	—		
(9)	W.Q. 1000°C. ...	20·4	43·7	41·5	59·2	170	98	88	90
	W.Q. 1150°C. ...	17·2	38·4	62·0	74·4	156	120	120	117
(10)	W.Q. 1000°C. ...	24·0	46·8	35·0	52·2	196	53	51	50
	W.Q. 1150°C. ...	20·0	44·6	46·0	61·5	196	97	95	99
(11)	W.Q. 1000°C. ...	34·8	47·6	36·0	54·6	207	67	72	70
	W.Q. 1150°C. ...	27·2	44·0	53·0	68·8	179	120	108	112
(12)	W.Q. 1000°C. ...	37·9	49·6	27·0	40·5	217	30	26	50
	W.Q. 1150°C. ...	32·9	47·6	35·0	52·2	207	47	49	53
(13)	W.Q. 1000°C. ...	—	47·8	28·5	44·6	217	42	50	42
(14)	W.Q. 1000°C. ...	29·6	43·0	38·0	62·2	166	99	105	109
	W.Q. 1100°C. ...	21·1	39·2	50·0	67·8	156	120	120	120
(15)	A.C. 1050°C. ...	33·2	49·0	35·0	49·0	—	—		
(16)	A.C. 1050°C. ...	24·2	47·7	35·5	50·0	—	—		
(17)	A.C. 1050°C. ...	33·8	53·2	26·0	31·0	—	—		

(B) Chromium-Silicon Steels.

In almost every way, the effect of silicon on the structure and properties of chromium steels is the reverse of that of nickel. Silicon raises considerably the temperature of the carbon change point and reduces the air hardening capacity of the steel to which it is added. Like chromium, silicon

also raises the temperature of the A.3 point and lowers that of A.4 so that eventually γ-iron ceases to exist in iron-silicon alloys when sufficient of this element is added. Indeed, its effect in this respect is considerably greater than that of chromium, for while gamma iron is produced in carbonless iron-chromium alloys until the chromium content reaches about 13 per cent., the corresponding limit for iron-silicon alloys is about 2·2 per cent. With these characteristics in mind, one would not expect silicon to have the range of usefulness, in connection with high chromium steels, that is possessed by nickel. The addition of silicon is not likely to lead to the production of austenitic steels ; on the contrary, one would expect it to accentuate the effects, observed in
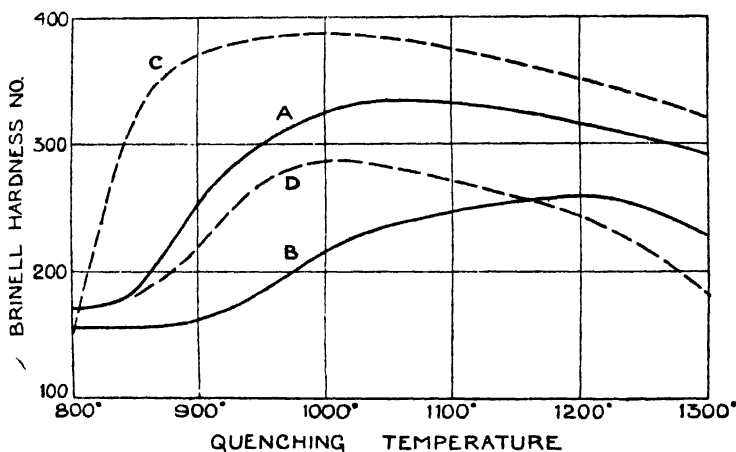
FIG. 132. Effect of about 1 per cent. silicon on the hardening of stainless iron.

Curve	Carbon %	Silicon %	Chromium %	Nickel %
A	0·12	0·89	11·5	0·42
B	0·10	1·0	15·4	0·54
C	0·09	0·23	12·3	0·23
D	0·10	0·36	15·5	0·39

irons containing more than about 15 per cent. chromium, which distinguish such irons from those with less than this amount, and also to cause these effects to be developed at lower chromium contents. This is actually the case, the effect of silicon on the properties of stainless irons containing up to about 15 per cent. chromium being very marked.

Plate XXVI

Fig. 133.   Stainless iron containing 12% chromium and 1·06% silicon, after oil quenching from 1,100°C.   × 100. Note presence of large amount of free ferrite

For example, the addition of about one per cent. silicon affects the hardening of irons containing 11·5 and 15·4 per cent. chromium, respectively, as is indicated in Fig. 132. These curves represent the Brinell hardness numbers of small samples which were water quenched from the temperatures indicated ; curves A and B refer to material containing about one per cent. silicon, C and D represent values similarly obtained from irons containing only a small amount of silicon but otherwise similar in analysis to A and B. The hardening of the lower chromium iron is much reduced by the silicon and this is accompanied by the presence, in the microstructure, of considerable amounts of ferrite ; thus, Fig. 133 reproduces the structure of an iron similar in analysis to A after quenching from 1,100°C. and one may note the large amount of ferrite visible. For comparison, a low silicon iron of the same chromium content consists entirely of martensite when quenched from any temperature between 950° and 1,150°C. The presence of rather less than one per cent. silicon has, in fact, produced a material similar, as regards hardening capacity, to a low silicon iron containing two or three per cent. more chromium. Similarly, the iron containing 15·4 per cent. chromium and 1·1 per cent. silicon behaves, when quenched, in a manner very much like that of the stainless iron containing 17·2 per cent. chromium and figured in curve E, Fig. 34.

Fig. 134 shows the effect of 3·0/3·5 per cent. silicon on the hardening of low carbon material of different chromium contents, and again comparable results are given from material low in silicon but otherwise similar in analysis. The influence of chromium content is also evident here for whereas the Ac.1 change occurs at 950°C. or thereabouts in the high silicon material with 8·7 per cent. chromium, a temperature of 1,050°C. is required for hardening when the chromium is raised to 14·9 per cent. In the latter case also, the maximum hardness attained is only 277 in spite of the rather higher carbon content of the material.

Fig. 135 refers to steels containing about 0·5 per cent. carbon ; the higher silicon sample hardens well but it requires a considerably higher temperature than the other to produce the same hardening effect and also the same solution and diffusion of the carbide, an important matter from the point of view of resistance to corrosion. A study of Figs. 132 to 135

indicates that the effect of silicon on the temperature of the Ac.1 change varies to some extent with the chromium content and probably with that of carbon as well. In the case of material containing 12/14 per cent. chromium, however, the
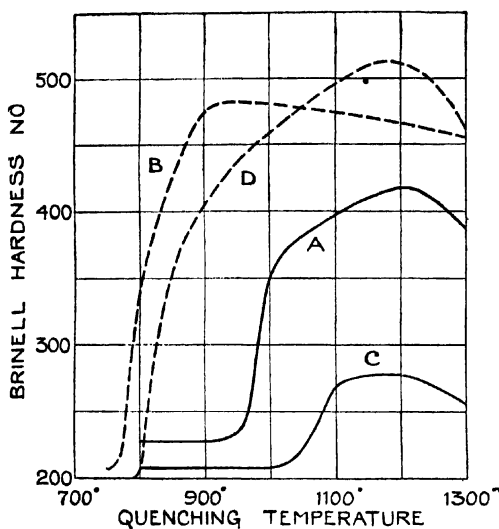

FIG. 134. Effect of 3·0/3·5 per cent. silicon on the hardening of stainless steels.

Curve	Carbon	Silicon	Chromium	Nickel
	%	%	%	%
A	0·15	3·5	8·7	0·47
B	0·18	0·15	8·8	0·92
C	0·22	3·3	14·9	0·64
D	0·29	0·04	14·2	0·2

temperature is raised 45/50°C. by each per cent. silicon, up to 4 or 5 per cent.

The effect of silicon, apart from that of raising the hardening temperature, is noticeable in two directions on the mechanical properties of high chromium steels. In the first place the silicon retards the tempering of the steel so that, when hardened and then tempered at 700°C. or thereabouts, the silicon steel is rather harder than a similar steel low in silicon ; secondly, under similar conditions of hardening and tempering, silicon is very liable to reduce the toughness of the material, often to a considerable extent. These effects are ·

well illustrated by the following series of results obtained at the Research Department, Woolwich Arsenal.*
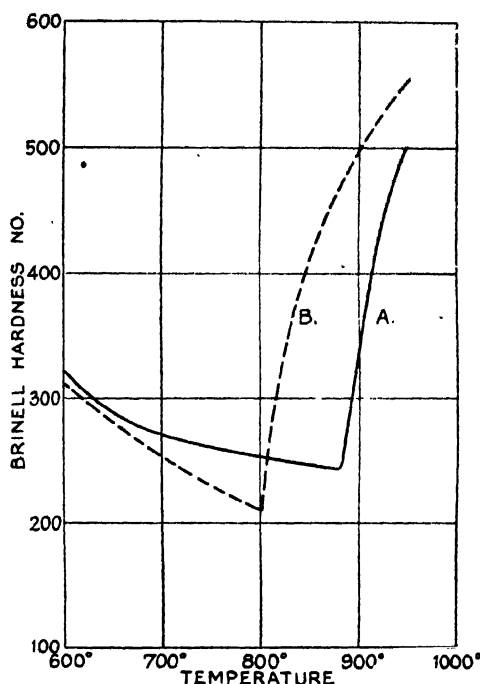
Fig. 135.   Effect of silicon on the hardening of stainless steels containing 0·5/0·55 per cent. carbon.

Curve	Carbon %	Silicon %	Chromium %
A	0·55	1·89	14·4
B	0·51	0·54	14·4

In this investigation, two grades of steels were used, with low carbon and high carbon respectively, and having the analyses given below :—

Mark.	Carbon	Silicon	Chromium
A.	0·15	0·11	13·5
B.	0·17	1·35	13·9
C.	0·31	0·31	14·2
D.	0·85	1·43	14·7

* " Metallurgical Data on Stainless Steels." H. H. Abram.   *Chem. & Met. Eng.*, Vol. XXX, p. 430 (1924).

Two series of tests were obtained. In the first series the bars were oil hardened at 950°C. and subsequently tempered at various temperatures. As, however, the high silicon steels were not effectively hardened from 950°C., a further series of test bars were oil hardened from 1,000°C. and then tempered at the same series of tempering temperatures as before.

The results obtained from these two 'series of tests are given in Tables XLVI and XLVII.

TABLE XLVI.

Influence of Silicon on the Mechanical Properties of Stainless Steel.

SERIES I. OIL HARDENED, 950° C.

Steel	Carbon. %	Silicon. %	Tempering Tempera-ture	Yield Point, tons per sq. Inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 Ins.	Reduc-tion of Area per cent.	Brinell Hard-ness Number.	Izod Impact, ft. lbs.		
A.	0·15	0·11	600° C.	50·5	59·8	21	63	285	27	29	26
			650° C.	39·5	49·4	24	66	283	37	38	41
			700° C.	32·4	43·6	28	69	206	109	103	109
B.	0·17	1·35	600° C.	30·2	46·2	27	62	229	9	10	8
			650° C.	30·0	44·5	27	64	222	14	13	13
			700° C.	27·5	42·2	32	67	210	15	14	14
C.	0·31	0·31	600° C.	54·0	65·4	18	55	305	31	33	24
			650° C.	43·0	55·6	23	60	262	39	35	37
			700° C.	35·0	48·7	28	67	228	64	68	68
D.	0·35	1·43	600° C.	49·0	62·7	19	54	296	13	13	14
			650° C.	44·5	58·8	22	55	274	16	18	16
			700° C.	38·5	53·7	27	59	249	24	23	23

The first series of tests shows very clearly the embrittling effect of the silicon but does not show the hardening effect so well because the high silicon steels (especially that containing the lower carbon) were not fully hardened. Series II, however, shows the hardening effect very well.

Values for Young's Modulus of Elasticity were also obtained from these four steels and they indicate that silicon has no noticeable effect on the elasticity of the steel. The mean values for each steel after hardening and tempering are given in Table XLVIII.

TABLE XLVII.

Influence of Silicon on the Mechanical Properties of Stainless Steel.

SERIES II.   OIL HARDENED, 1,000° C.

Steel.	Carbon, %	Silicon. %	Tempering Temperature.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Brinell Hard-ness Number.
A.	0·15	0·11	600° C.	47·0	57·0	22	68	317
			650° C.	40·0	50·0	25	65	280
			700° C.	32·5	43·8	29	67	244
B.	0·17	1·35	600° C.	44·5	57·6	22	57	276
			650° C.	39·5	53·6	24	60	259
			700° C.	35·5	49·8	27	61	238
C.	0·31	0·31	600° C.	54·0	67·7	19	50	317
			650° C.	45·0	59·4	23	56	280
			700° C.	37·0	52·2	26	62	244
D.	0·35	1·43	600° C.	55·0	69·7	19	50	326
			650° C.	50·0	65·1	21	58	301
			700° C.	42·5	58·2	24	57	270

TABLE XLVIII.

Effect of Silicon on the Modulus of Elasticity of Stainless Steel.

Steel.	Carbon. %	Silicon. %	Chrom-ium. %	SERIES I. O.H. 950° C. and tempered. Lbs. per sq. inch.	SERIES II. O.H. 1,000° C. and tempered. Lbs. per sq. inch.
A.	0·15	0·11	13·5	$31·5 \times 10^6$	$30·9 \times 10^6$
B.	0·17	1·35	13·9	$29·5 \times 10^6$	$29·6 \times 10^6$
C.	0·31	0·31	14·2	$32·2 \times 10^6$	$32·0 \times 10^6$
D.	0·35	1·43	14·7	$32·4 \times 10^6$	$31·6 \times 10^6$

Generally speaking, the presence of any considerable amount of silicon in hardenable stainless steel, containing 12 per cent. chromium is uncommon. It raises considerably the temperature necessary for hardening and in no way does it improve the hardening capacity of the steel, rather the reverse; hence its presence is obviously undesirable in material where the ability to harden, and that without the

necessity of quenching from unduly high temperatures, are properties of first rate importance. It is more frequently found in stainless irons in quantities up to about one per cent., or rather more, and is there either as an intentional component or inadvertently as a result of steel making conditions involving the use of ferrosilicon as a reducing agent. The mechanical properties of a 12 per cent. chromium stainless iron, containing approximately one per cent. silicon, are set out in Table XLIX. The fully tempered material is tough, but the hardened forms possess appreciably lower impact values than the irons low in silicon and listed in Tables I to III, pages 101 to 104.

TABLE XLIX.

Mechanical Properties of Stainless Iron containing 1 per cent. Silicon.

(Bars treated : $1\frac{1}{8}''$ diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·12	1·08	0·20	12·1	0·35

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Brinell Hardness Number. Hard'd	Temp'd	Izod Impact, ft. lbs.		
A.H. 950°C. ...	38·0	50·6	20·0	41·9	196		5	5	5
,, 1000°C. ...	36·4	55·2	19·0	36·4	228		5	4	4
O.H. 950°C. ...	56·8	71·6	12·5	26·1	286		14	11	12
,, W.Q. 500°C.	59·6	74·8	20·5	48·5	302	302	2	2	2
,, W.Q. 600°C.	36·4	48·8	25·5	59·3	286	217	41	38	44
,, W.Q. 700°C.	31·0	42·8	30·5	60·4	302	196	74	60	59
,, W.Q. 800°C.	27·8	40·6	32·0	58·0	295	179	78	85	89

The effect of about one per cent. silicon on the toughness of fully tempered irons of about this chromium content appears to vary in a manner not predictable from composition. Some casts of this material give good impact values ; others of similar analysis give low values. The cause of the varia-tion is obscure as the steels may be made under apparently .

identical conditions. Thus the following tests were obtained from a series of casts made during the course of one week in a 7-ton electric furnace. The bars tested were one inch in diameter, and were hardened in oil from 950°/975°C. and subsequently tempered at 700°C.

Cast.	Carbon %	Silicon %	Chro-mium %	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Izod Impact, ft. lbs.		
R 1005	0·11	0·89	12·5	30·4	44·0	25·0	52·2	77	67	67
R 1008	0·09	0·77	12·0	35·2	42·6	30·0	67·8	104	105	102
R 1010	0·09	1·06	12·4	30·0	40·0	30·0	59·3	78	97	77
R 1012	0·12	1·08	12·1	31·0	42·8	30·5	60·4	74	69	59
R 1014	0·14	1·08	12·2	30·0	43·6	33·0	64·8	28	25	27

The first four casts were relatively tough, although their actual toughness values varied; the fifth, made apparently under the same conditions, gave a very much lower impact value.

The addition of a similar amount of silicon to irons containing 14 per cent. or more chromium results in the production of relatively brittle material, as judged by the Izod test. As has been shown earlier in these pages, the plain chromium irons, containing more than about 15 per cent. are likely to have low impact values, no matter how they are treated. The addition of one per cent. silicon does not improve these values, if anything it tends to make them worse, and it lowers the chromium content at which the

TABLE L.

Effect of Silicon on the Mechanical Properties of High Chromium Irons.

Carbon	Silicon	Chro-mium %	Treatment.	Brinell Hardness Number. Hard'd	Temp'd	Izod Impact, ft. lbs.	
0·10	1·10	15·5	W.H. 950°C., W.Q. 700°C.	163	166	2	2
			W.H. 1050°C.. W.Q. 700°C.	217	187	3	3
0·18	0·90	17·5	W.H. 950°C., W.Q. 700°C.	166	168	4	5
			W.H. 1050°C., W.Q. 700°C.	228	194	6	7

brittleness is produced. The values given in Table L were obtained from bars ⅜ inch square, rolled from 12 inch square ingots, and they indicate the type of impact value to be obtained even under these ideal conditions. All the fractures were coarsely crystalline.

The addition of higher percentages of silicon lowers still further the chromium content at which low carbon steels lose their toughness, and it does not improve the properties of those of higher chromium content which already possess low impact values when containing little or no silicon ; as witness the tests in Table LI. All the impact fractures of these bars were coarsely crystalline.

TABLE LI.

Effect of High Silicon Content on Stainless Irons.

(Bars treated : ½″ square.)

Carbon %	Silicon %	Chromium %	Treatment.	Brinell Hardness Number.		Izod Impact, ft. lbs.	
				Hard'd	Temp'd		
0·15	3·5	8·7	W.H. 950°C., W.Q. 700°C.	228	228	4	4
			W.H. 1050°C., W.Q. 700°C.	364	282	4	4
			A.H. 1050°C., W.Q. 650°C.	241	235	3	4
0·22	3·3	14·9	W.H. 950°C., W.Q. 700°C.	228	228	2	3
			W.H. 1050°C., W.Q. 700°C.	235	228	2	2

From several points of view the properties induced in stainless iron by the presence of about one per cent. silicon would be useful. Thus although such irons, containing 12/14 per cent. chromium, do not air harden to anything like the same extent as the higher carbon steels of similar chromium content, they possess this characteristic in some degree and the reduction of even this limited capacity for air hardening would be valuable for certain purposes. For example, in the engineering application of stainless materials, the stainless irons may be looked upon as taking the place of ordinary mild steel. The latter material is particularly fool-proof in its ability to withstand maltreatment during fabrication by various workshop processes ; thus it does not air-harden in the least, it is not greatly affected by a

considerable amount of overheating and it may readily be worked over a considerable range of temperature. The more nearly a stainless iron approaches ordinary mild steel in these respects, the less difficulty is there likely to be in developing its engineering uses. Now the possession of air-hardening properties, even in relatively small degree, is a distinct disadvantage in several respects. Tempering is necessary after cooling from forging heats, not only to remove the hardness thus produced—quite frequently, this increased hardness, in the case of stainless iron, would not be sufficient to cause any trouble in machining operations—but to restore ductility and toughness to the material. If this were not done, such operations for example, as the cold pressing, flanging or bending of plates would be likely to lead to cracked material. For the same reason, air-hardening properties are undesirable in material for rivets ; they entail the latter being driven at tempering heats, otherwise the rivet heads will most probably fly off. The action of silicon in diminishing air-hardening effects and in raising the temperature at which they begin to be noticeable would therefore be useful were it not for the fact that these desirable attributes are accompanied and entirely overshadowed by the liability to brittleness, after any form of treatment, which is characteristic of silicon-containing material. Hence, when tough material is essential, the presence of silicon is undesirable. This is recognised, for example, in specifications for aircraft material in which the silicon content of stainless iron and steel is limited to not more than 0.5 per cent.*

Owing possibly to the fact that the impact test is used much less frequently in the United States of America than in Great Britain, stainless irons containing silicon have been widely used there. For example, large quantities of low carbon material containing about 17 per cent. chromium and 1 per cent. silicon have been employed for the construction of plant for the manufacture and handling of nitric acid. From a corrosion resisting point of view, such material may be eminently satisfactory,† but its intrinsic brittleness is not regarded favourably by chemical engineers

* E.g., British Engineering Standards Specifications S.61, S.62, S.80 ; also D.T.D. Specifications Nos. 23, 39, 46, 53, issued by the Air Board.

† But see page 303, re the effect of high silicon content on the rate of attack of nitric acid.

in this country, with the result that it has been little used here.

It may be objected that as plates are not usually notched, an impact test does not reproduce service conditions, the latter being more nearly represented by ordinary bend tests ; and, when tested in this way, the high silicon stainless iron may give quite good results. There may be some point in this, but on the other hand, rivets certainly possess re-entrant angles and it is a fact that very great trouble was experienced in the United States in successfully driving rivets of this material ; at first, the rivet heads were liable to fly off in a most disconcerting manner with little or no provocation. Actually, some six months elapsed before a special technique was developed by which fairly satisfactory rivets could be driven. When it is remembered that such rivets should be specially designed to avoid a sharp angle under the head, that the holes in the plates require to be countersunk and reamered out for the same reason and to avoid grooving the rivets and that the latter can only be successfully driven in the boiler shop and not on the plant site, as they must not be heated above 760°C. or they will be too hopelessly brittle, it will be realised that the material is far from ideal for fabrication into plant by boilermakers' methods. English chemical engineers are probably wise in preferring tougher material for their equipment.

The greatest commercial value of the chromium-silicon alloys appears to lie in their superior resistance to oxidation at high temperatures as compared with steels containing similar amounts of chromium but negligible amounts of silicon. For this reason, they have found use for such a purpose as exhaust valves for internal combustion engines where temperatures of 800°C. or over are likely to be reached. In this particular case, they have also the added advantage that, owing to the effect of the silicon in raising the temperature at which the carbon change point occurs, they are less liable to reach, in service, a temperature from which they would harden on cooling. Obviously, if a valve reaches such a temperature in use, it is likely to harden on cooling when the engine is stopped. On restarting the engine after it has become cold, there is a possibility that a valve so hardened may break. Examples of valve failures due to

this cause were quoted by Aitchison.* though it is probable that they occur only very rarely.

For such purposes as this it is not necessary to use so high a chromium content as that in ordinary stainless steel ; 6/8 per cent. is ample and this amount, in combination with about 1 per cent. silicon and 0·5 per cent. carbon gives a material which may be used up to about 850°C. and at the same time possesses very good physical properties.   The latter point is illustrated by the tests given in Table LII and obtained from bars 1⅛ inch in diameter made from different casts of steel having approximately the above analysis :—

TABLE LII.

Mechanical Properties of Steels containing 7 per cent. Chromium and 1 per cent. Silicon.

Cast.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.
A.	A.H. 900°C., W.Q. 750°C.	40·8	52·6	28·0	61·5	251	49 47 44
B.	,, ,,	40·8	52·0	28·0	66·8	255	61 60 58
C.	,, W.Q. 700°C.	44·8	58·2	22·0	49·7	286	29 29 24
	,, W.Q. 750°C.	46·0	54·6	23·0	53·4	262	49 40
D.	,, W.Q. 700°C.	52·0	57·8	25·0	55·8	269	35 30
	,, W.Q. 750°C.	40·4	53·8	25·0	57·0	255	57 85 51

The valves of the engine fitted to the Vickers-Vimy aeroplane used by Sir A. W. Brown and Sir J. Alcock for their epoch-making flight across the Atlantic on June 14th, 1915, were made of steel of this type and the fact that they behaved perfectly under the arduous conditions of that flight is evidence that the steel has eminently suitable properties for such valves.

If resistance to oxidation at still higher temperatures is required, the silicon content of the steel may be increased to 2 or 3 per cent., the chromium remaining at about 8 per cent.   Material of this analysis is very resistant to oxidation at any temperature up to about 1,000°C. ; in addition, it is not capable of being hardened by rapid cooling until a

* "Valve Steels for Internal Combustion Engines." L. Aitchison. *Proc. Inst. Auto. Eng.*, Vol. XIV (1919), p. 31.

temperature nearly as high as this is reached. This is illustrated by the curves in Fig. 186, which show the Brinell hardness numbers obtained from small samples of such a steel after water quenching or air cooling from a series of gradually increasing temperatures. These curves also illustrate very strikingly the effect of silicon in reducing the
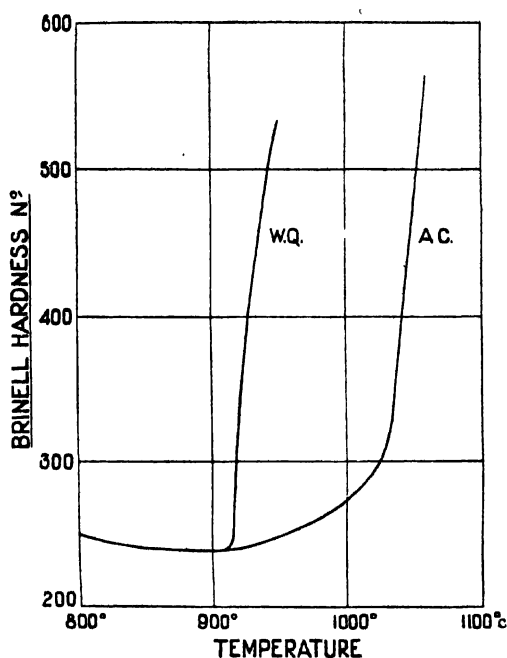
FIG. 136. Brinell hardness numbers obtained from small samples of steel containing 0·43 % carbon, 3·29 % silicon, 0·24 % manganese and 7·4% chromium after water quenching (W.Q.) or air cooling (A.C.) from the temperatures indicated.

air-hardening capacity of the steel to which it is added. With such a high silicon content, however, the effect of this element on the mechanical properties of the steel becomes very evident; such steels, when hardened and fully tempered, are considerably harder than steels low in silicon but otherwise similar in analysis; they also give low Izod impact values. Typical properties are shown in Table LIII.

These values should be compared with those given by

TABLE LIII.

Mechanical Properties of High Silicon Valve Steels.

(Bars treated : $1\frac{1}{8}''$ diameter.)

No.	Carbon %	Silicon %	Chromium %
(1)	0·51	3·17	8·0
(2)	0·61	3·2	8·5
(3)	0·43	3·29	7·4

No.	Treatment.	Yield Point, tons per sq. inch	Maximum Stress, tons per sq. inch	Elongation per cent. on 2 ins.	Reduction of Area per cent	Brinell		Izod Impact, ft. lbs.
						Hard'd.	Temp'd.	
(1)	O.H. 1000°C., W.Q. 800°C.	50·4	62·8	22·0	40·6	555	293	8 8
	A.H. 950°C., W.Q. 750°C.	34·0	54·4	26·0	45·9	255	255	1 1
(2)	O.H. 1000°C., W.Q. 700°C.	60·0	74·6	15·0	26·1	600	364	2 3
(3)	O.H. 950°C., W.Q. 700°C.	34·8	52·0	27·0	47·2	—	—	2 1

the lower silicon alloy mentioned earlier (Table LII) and also by the chromium steel of similar carbon content listed in Table IX, page 109.

The mechanical tests on these high silicon valve steels have been given for the sake of completeness. It does not necessarily follow, however, that the use of material containing two or three per cent. silicon for the manufacture of valves is to be deprecated because it has such a low impact value at ordinary temperatures. Large numbers of valves made of such steel and also of other types possessing equally low impact values, have been put into service during the last ten or fifteen years and a broken valve is an exceedingly rare occurrence Most probably the reason may be found in the fact that a valve, during the greater part of its working life, is heated considerably above atmospheric temperature, and the impact value of these steels increases rapidly when they are heated. Thus the figures given in Tables LIV were obtained by Henshaw[*] on a steel of this type and they show that it possesses a high degree of toughness at a low red heat. Failure owing to brittleness is not likely to occur,

[*] " Valve Steels." *Journ. Roy. Aero. Soc.*, March, 1927. The figures quoted refer to a steel containing some tungsten but they may be applied to the plain chromium-silicon steel.

therefore, during service but it may happen when the engine is cold. The author has known a valve of this steel to break when it was accidentally dropped during the overhaul of an engine. This particular valve had been in service for a considerable time under severe conditions and had developed shallow " heat cracks " on the stem, close to the head. One of these cracks, acting as a notch, gave the necessary lead to the fracture.

TABLE LIV.

Impact Tests of High Silicon Valve Steel at High Temperatures.

Carbon 0·54 per cent. ; Silicon 2·5 per cent. ; Chromium 8·2 per cent. ; Tungsten 1·96 per cent.

Temperature.	Impact Value ft. lbs.
15°C.	4
100°C.	7
200°C.	18
300°C.	36
400°C.	36
500°C.	36
600°C.	38
700°C.	50
800°C.	74
900°C.	77

For heat resisting purposes, alloys with about 5 per cent. each silicon and chromium have been proposed. Alloys of this composition require to be heated to about 1,000°C. before they may be hardened by quenching, a feature of value for articles which are likely, in use, to be repeatedly heated to and cooled from temperatures approaching this value. Such alloys as these, and also the 8 per cent. chromium, 3 per cent. silicon type described above, do not resist oxidation at temperatures as high as do the nickel-chromium alloys of the " nichrome " or other types, nor do they possess as great a strength at high temperatures as the latter alloys ; they are, however, very much cheaper than the nickel-chromium type and are more easily worked. They will obviously be of value where the oxidation resistance and

strength at high temperatures which they possess are ample for the purpose required.

(C) Chromium-Manganese Steels.

As a general rule, stainless steels do not contain large amounts of manganese.   Frequently there is not more than 0·1/0·8 per cent. in the hardenable varieties and rarely does the figure exceed 1 per cent.   F. M. Becket obtained a patent[*] in 1920 for steels containing 10/45 per cent. chromium, 8/25 per cent. manganese and up to 8 per cent. each carbon and silicon and claimed that such steels were machinable, responded readily to heat treatment, resisted oxidation at high temperatures and had a low magnetic permeability. Five years later, M. Baeke was granted a patent[†] in France
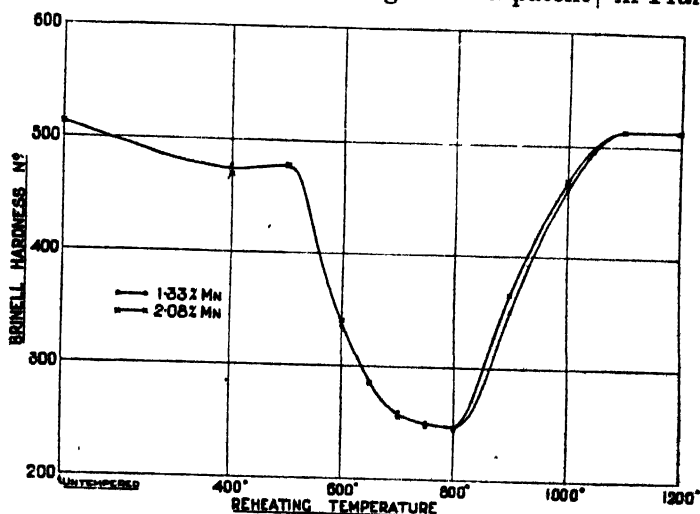
FIG. 137.   Effect of manganese on the hardening and tempering of stainless steel.

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0·26	1·00	1·33	14·6	0·33
0·26	0·91	2·06	14·6	0·33

for steels containing 8/25 per cent. chromium, 2/24 per cent. manganese and 0·4/1·5 per cent. carbon ; these were stated to be very resistant to acids and alkalies and to be unattacked by air.   The author is not aware of the commercial development of steels of these types.

* U.S. patent 1,333,151 (March 3rd, 1920).

† French patent 595,530 (March 20th, 1925).

The results of experiments with regard to the effect of manganese, up to 2 per cent., on the hardening of 14 per cent. chromium steel are plotted in Fig. 137, the steels being first hardened and then reheated to gradually increasing temperatures; the samples were quenched out from each tempering heat and their Brinell hardness values then determined.   The steels unfortunately contained more silicon than is desirable, but if allowance be made for the effect of one per cent. of this element in raising the temperature of Ac.1 45/50°C., it would appear that the presence of two per cent. manganese has no great effect on the position of the carbon change point on heating, nor does it modify to any appreciable extent the tempering of the hardened samples.   In this respect, it has a similar action, or lack of it, to that which it has on ordinary carbon steel.   It may be concluded that the presence of one or two per cent. manganese does not necessitate any modification in the heat treatment of a hardenable stainless steel containing 14 per cent. chromium or thereabouts.   Also mechanical tests on the steels whose hardening and tempering character-istics are plotted in Fig. 137 showed no appreciable effect on the properties of the steel due to this manganese content.

These two steels showed no evidence of the retention of austenite even after quenching from 1,200°C. ; with a higher content of manganese, however, this constituent is obtained in quenched samples.   Thus steels containing the following amounts of carbon, manganese and chromium :—

	A.	B.	C.	D.
Carbon % ...	0·70	1·08	0·43	0·58
Manganese % ...	3·2	5·1	5·3	6·7
Chromium % ...	14·1	14·9	14·8	12·8

were austenitic when quenched from high temperatures, e.g., 1,100°C. and 1,200°C., though they were partly marten-sitic after reheating to and cooling from 800°/1,000°C., their behaviour in this respect being typified by the curves in Fig. 138.   They were also almost unmachinable.

Recently F. M. Becket has published the results[*] of an investigation into the properties of austenitic chromium-

* "Chromium Manganese Steels." *Amer. Iron & Steel Inst.*, May, 1930.

manganese steels of low carbon content.   His results, given
in Table LV, indicate that a minimum of about 10 per cent.
manganese is required, in a steel containing 17/18 per cent.
chromium, in order to produce a material having properties
similar to those of the austenitic chromium-nickel steels.
It should be noted that the low carbon steels were not com-
pletely austenitic ; they also contained ferrite (in a manner
similar to Fig. 125) in amounts which increased as the
quenching temperature rose above 1,000° C.
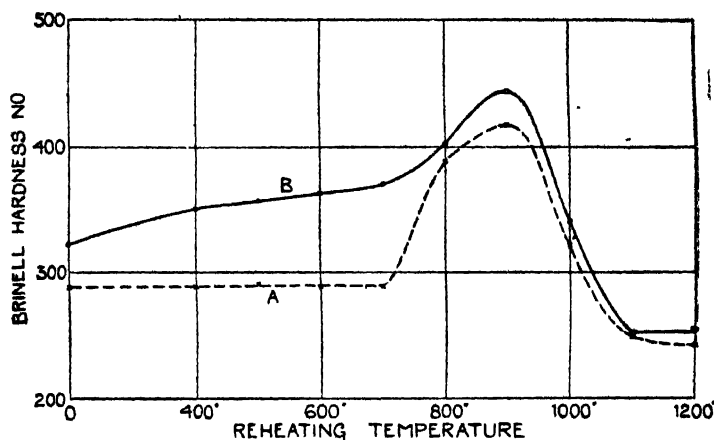
FIG. 138.   Relation between reheating temperature and Brinell hardness
of chromium-manganese steels ; samples water quenched from each tem-
perature.

Curve	Carbon %	Silicon %	Chromium %	Nickel %
A	0·53	6·7	12·8	0·42
B	1·08	5·1	14·9	0·40

The fact that manganese behaves, as regards the forma-
tion of austenite, in much the same way as nickel suggests
that it might also possess a further similarity with the latter
metal in increasing the hardening capacity and toughness
of low carbon irons and steels containing 16/20 per cent.
chromium.   Actually the addition of 1 or 2 per cent. man-
ganese to an iron containing 16/17 per cent. chromium does
slightly increase the hardness of the latter after quenching,
as indicated in Fig. 189, but the difference is not great.
Much the same effect is produced with material of similar
chromium, but rather higher carbon, content which hardens
to a limited extent.   Here, the presence of 1 or 2 per cent.

TABLE LV.

Mechanical Properties of Chromium-Manganese Steels.

No.	Carbon %	Silicon %	Manganese %	Treatment	Yield Point, tons per sq. inch	Maximum Stress, tons per sq. inch	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness No.	Izod Impact ft. lbs.
(1)	0·06	17·47	6·48	W.Q. 1000°C.	19·2	49·1	21·0	25·0	149	94
				W.Q. 1150°C.	21·0	44·5	26·0	31·0	163	103
(2)	0·07	17·88	8·26	W.Q. 1050°C.	21·4	54·2	27·0	28·0	163	112
				A.C.	23·2	56·3	25·0	25·0	156	77
				A.C. 1150°C.	18·3	48·9	27·0	27·0	156	120
				A.C. "	21·4	53·6	24·0	22·0	163	120
(3)	0·07	17·55	10·48	W.Q. 1050°C.	21·0	47·3	40·0	40·0	163	120
				A.C.	21·0	57·6	37·0	32·0	174	111
				1150°C.	23·1	41·5	40·0	42·0	147	112
				A.C.	21·4	48·2	38·0	36·0	149	85
(4)	0·09	17·54	14·77	W.Q. 1050°C.	22·6	43·2	49·0	66·0	163	120
				A.C.	19·6	47·3	51·0	60·0	166	120
				W.Q. 1150°C.	24·0	40·1	45·0	70·0	166	120
				A.C. "	23·2	45·5	42·0	54·0	163	116
(5)	0·05	17·88	16·53	W.Q. 1050°C.	21·0	45·5	49·0	69·0	174	120
				W.Q. 1150°C.	24·6	42·7	50·0	71·0	173	120
(6)	0·10	20·41	11·44	W.Q. 1050°C.	21·9	43·8	43·0	51·0	163	120
				A.C. "	21·0	48·5	38·0	45·0	163	85
(7)	0·22	16·93	7·62	W.Q. 1050°C.	20·5	54·0	21·0	31·0	207	63
(8)	0·18	18·34	11·75	W.Q. 1050°C.	21·3	60·2	51·0	65·0	217	85
				W.Q. 1150°C.	21·3	53·6	48·0	43·0	187	120
(9)	0·25	19·13	13·64	W.Q. 1050°C.	20·1	63·9	45·0	41·0	183	116
				W.Q. 1150°C.	21·0	58·5	47·0	37·0	166	116
(10)	0·26	18·08	20·25	W.Q. 1050°C.	23·2	46·0	51·0	57·0	179	74
				W.Q. 1150°C.	20·5	40·9	50·0	53·0	170	120

manganese increases in some measure the hardness after quenching and thereby improves the mechanical properties of the subsequently tempered material. Examples are
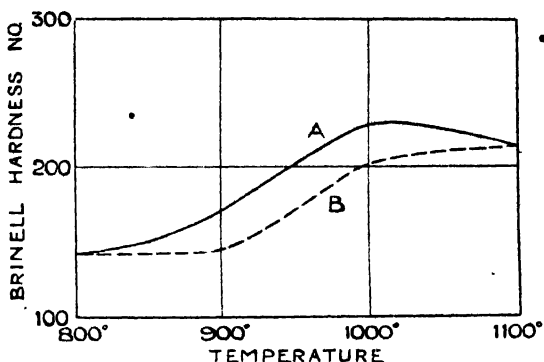
FIG. 139. Effect of manganese on the hardening of stainless iron.

Curve	Carbon %	Manganese %	Chromium %	Nickel %
A	0·11	1·22	16·1	0·19
B	0·10	0·17	16·0	0·20
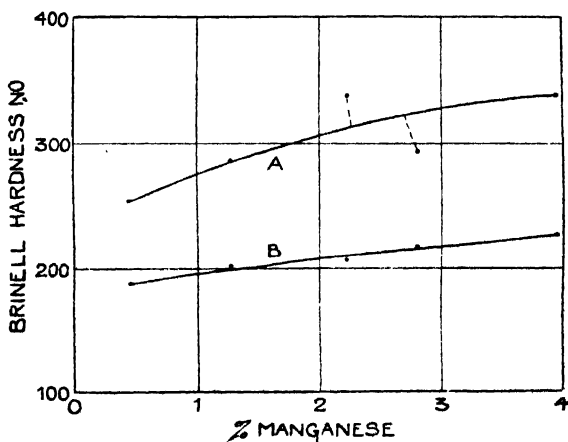
FIG. 140. Effect of manganese on 18/19 per cent. chromium steel (carbon 0·21/0·23 per cent.) :—

Curve A. Hardness values of 3 in. square ingots air cooled after casting.

Curve B. Hardness values of bars, 1¼ in. diam., air cooled from rolling heat, 1,000/1,100° C.

given in Table LVI. That the effect is slight is evident, however, if a rather higher chromium content be used; in this case, even the presence of 4 per cent. manganese is not effective in making the steel harden to any notable extent; see Tables LVII and Fig. 140.

TABLE LVI.

Effect of Manganese on 17 per cent. Chromium Steel.

Treatment : O.H. 950°C., W.Q. 700°C.

(Bars treated : 1⅛" diameter.)

Carbon %	Man-ganese %	Chro-mium %	Nickel %	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Brinell as Hardened	Izod Impact, ft. lbs.
0·28	0·25	16·8	0·24	30·0	42·0	27·0	58·2	311	38 37 41
0·28	1·15	16·9	0·38	42·0	53·4	21·0	49·7	444	60 48 57
0·22	0·36	16·8	0·22	30·0	38·6	29·0	57·0	269	45 41 50
0·22	2·22	17·0	0·38	36·0	49·2	23·0	51·0	387	47 52 .

TABLE LVII.

Effect of Manganese on 18/19 per cent. Chromium Steel.

Treatment : O.H. 950°C., W.Q. 700°C.

(Bars treated : 1⅛" diameter.)

Carbon %	Man-ganese %	Chro-mium %	Nickel %	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Brinell as Hardened	Izod Impact, ft. lbs.
0·23	0·44	18·6	0·27	17·9	35·0	31·0	57·0	194	12 15 15
0·28	1·27	19·1	0·27	20·6	36·4	32·0	57·0	207	22 20 14
0·22	2·23	19·0	0·27	24·0	40·5	29·5	49·7	241	34 25 25
0·22	2·80	18·7	0·27	19·7	38·2	28·5	51·0	202	12 13
0·21	3·96	18·6	0·27	23·0	38·4	25·5	40·5	187	28 18 21

Manganese is an almost essential constituent of ordinary carbon steel and of most structural alloy steels, its presence being necessary to ensure soundness in the material and to prevent the sulphur in the steel producing hot working troubles; it also influences considerably the hardening capacity of the steel. On none of these counts does

manganese appear to be so necessary in high chromium steels. Perfectly sound ingots of the latter may be made even though the manganese content be 0·10 per cent. or less.   As regards sulphur, mention has already been made of the fact that this element appears to exist in high chromium steels in a different fashion from that in ordinary steels.   It is at least certain that stainless steel containing 0·07/0·10 per cent. sulphur and 0·1/0·2 per cent. manganese forges perfectly without the least sign of redshortness, although most steelmakers would look askance at such a combination in ordinary steels.*   On the third count, that of influencing hardening capacity, Tables LVI and LVII suggest that the effect of manganese is much less marked on high chromium steels than on less alloyed material.

Similarly, chromium-nickel steels of the " V.2.A." type, do not usually contain more than about 0·7 or 0·8 per cent. manganese but in the higher nickel alloys (e.g., containing 20 per cent. or more) it is often found to the extent of one or two per cent., presumably because its presence is beneficial from a forging point of view.

(D). Chromium-Copper Steels.

Copper is not generally present in the ordinary " cutlery" type of stainless steel nor in the stainless irons, but as it has certain definite effects from a corrosion resisting point of view, when added to such steels and irons, it is interesting to note its general effect on their physical properties.

In curve A, Fig. 141, are plotted the Brinell hardness numbers obtained on tempering at gradually increasing temperatures hardened samples of a 12 per cent. chromium steel to which had been added 1·2 per cent. copper.   The samples had been hardened by cooling freely in the air from 950°C, and from each tempering heat were quenched in water.   Curve B gives the results similarly obtained on a steel free from copper but otherwise identical in analysis, except that its carbon content was somewhat lower, 0·16 per cent. instead of 0·22 per cent.   A comparison of the curves indicates that the presence of 1·20 per cent. copper lowers the Ac.1 point about 25°C., a figure confirmed by thermal

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* According to F. R. Palmer (*Trans. A.S.S.T.*, December, 1928, p. 877), the hot working of stainless iron becomes seriously affected if the sulphur content exceeds 0·15 per cent., and material containing 0·20 per cent. and over is commercially unworkable.

analysis. Allowing for the difference in carbon content of the two steels, it would also appear that copper increases slightly the hardness of the steel when the latter is tempered at 600°C. or above. The difference, however, is not great.
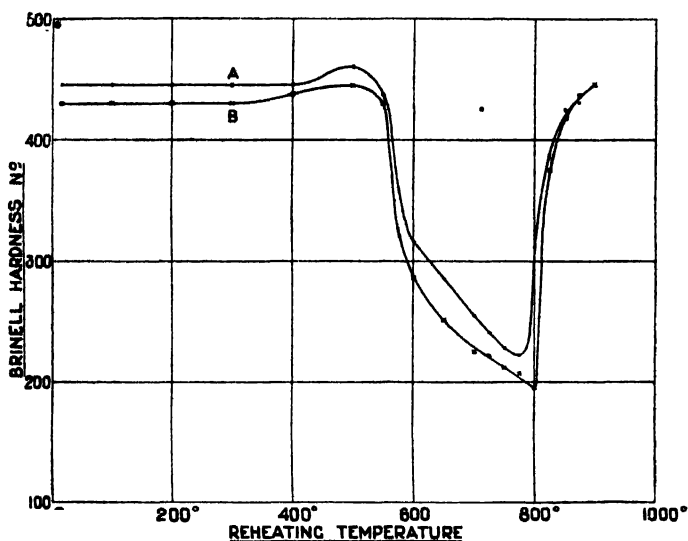
Fig. 141. Effect of copper on the hardening and tempering of stainless steel :—

Curve.	Carbon, %	Chromium, %	Copper, %
A.	0·22	12·1	1·20
B.	0·16	12·1	0·08

It would thus appear that copper acts in a somewhat similar manner to nickel but to a much less degree. The effect of about 1 per cent. copper is in fact so slight that its presence would not necessitate any modification of the ordinary methods of heat treatment of stainless steels.

On the other hand, the effect of copper differs from that of nickel in that the presence of fairly large amounts of the former metal does not lead to the production of austenite. Thus samples of the following alloys :—

	A	B
Carbon	0·17%	0·16%
Silicon	0·33%	0·33%
Manganese ...	0·11%	0·11%
Chromium ...	14·0 %	15·7 %
Copper	5·0 %	9·85%

were not austenitic when quenched from any temperature up to 1.200°C., the Brinell hardness numbers of small samples after water quenching from various temperatures being plotted in Fig. 142. It would also appear from these curves that the lowering of the temperature of Ac.1 which was noticeable with 1·2 per cent. copper does not become more pronounced with larger amounts of this element.
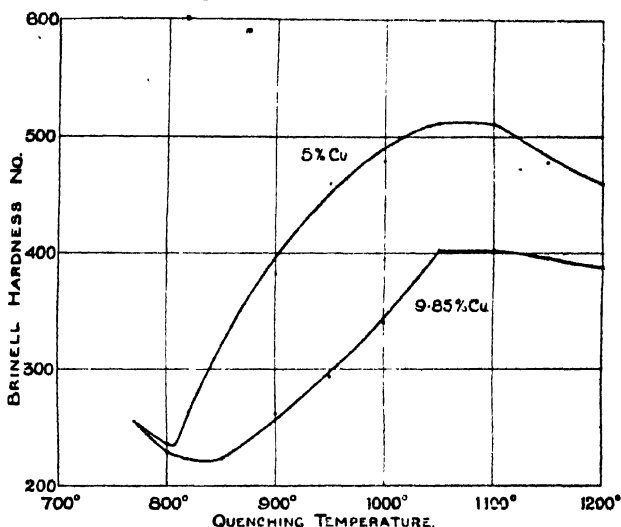
FIG. 142. Effect of high copper content on the hardening of stainless steel (see page 234 and compare with curve G. in Fig 35).

As the presence of small amounts of copper has occasionally been thought to exert a deleterious effect on the general properties of ordinary steel, it may be of interest to note that the steel mentioned on page 233, containing 1·2 per cent. copper, forged and rolled perfectly and that when hardened and tempered it was very tough; thus a bar, 1⅛ inches diameter, after being air hardened from 950°C. and then tempered at 700°C., gave a Brinell hardness number of 228 (corresponding to a tensile strength of 50 tons per square inch) and had an Izod impact value of 59 ft. lbs.

The tests in Table LVIII, quoted from a paper by Saklatwalla and Demmler,* also indicate that the addition of copper has a distinct hardening action on stainless iron but has no deleterious effects.

* *Trans. A.S.S.T.*, 1929, Vol. XV, p. 36.

TABLE LVIII.

Effect of Copper on Stainless Iron.

Carbon %	Chro-mium* %	Copper %	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Brinell Hard-ness Number.	Izod Impact, ft. lbs.
0·11	14·2	0·05	Annealed	18·7	31·9	40·0	78·0	146	94 96
0·12	13·3	1·30	,,	33·2	43·8	26·5	67·6	205	91 88

With regard to higher chromium steels, the Carpenter Steel Co. (U.S.A.) manufacture a steel containing approximately 0·30 per cent. carbon, 20 per cent. chromium and 1·0 per cent. copper. Material of this analysis does not harden to any great extent and it suffers from the disability of having a low impact value in the same way as steels of similar high chromium content but free from copper. Saklatwalla and Demmler give the data presented in Table LIX on such a steel.

TABLE LIX.

Effect of Copper on 20 per cent. Chromium Steel.

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Copper %
0·27	0·40	0·45	20·4	0·17	1·44

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Brinell Hard-ness Number.	Izod Impact, ft. lbs.
Annealed	23·3	43·5	22·0	52·6	215	2 1
W.H. 1000°C.,T. 425°C.	—	—	—	—	266	—
,, T. 600°C.	—	—	—	—	253	—

Very similar results were obtained on a steel of this type by Strauss and Talley* whose figures are quoted in Table LX. An interesting feature of their results and one difficult of explanation is the notable increase in impact value

* "Stainless Steels: Their Heat Treatment and Resistance to Sea-Water Corrosion." *Proc. A.S.T.M.*, 1924, Vol. 24, Pt. II.

obtained from samples quenched from high temperatures and not subsequently tempered. It should be noted that these Izod test pieces were machined with a round notch 0·079 inch (=2 mm.) diameter. The results are therefore not comparable with other impact test values quoted in this book. Tests on the British Standard test piece would have given lower values.

TABLE LX.

Effect of Copper on 20 per cent. Chromium Steel.

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Copper %
0·24	0·29	0·49	20·44	trace	1·08

Treatment.	Proportional Limit, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness No.	Izod Impact.† ft. lbs.
As received from steel maker	11·5	50·4	20·0	35·0	207	4 4
F.C. 870°C.	20·3	38·0	32·0	62·3	170	1 2
„ 982°C.	20·0	36·6	30·2	59·3	163	2 2
„ 1093°C.	18·0	35·8	28·5	59·5	163	1 1
„ 1204°C.	17·1	35·7	6·8	7·4*	170	1 1
W.Q. 871°C.	13·6	38·4	30·0	60·8	163	6 15
„ 982°C.	11·3	49·4	20·2	37·6	203	4 5
„ 1093°C.	11·3	54·0	19·2	31·4	187	25 23
„ „	10·5	52·5	13·0	10·7*	—	33 33
„ 1204°C.	11·3	45·5	29·7	26·0	174	31 27
W.Q. 982°C., A.C. 538°C. ...	29·7	55·1	2·8	2·8*	228	1 1
W.Q. 1093°C., A.C. 538°C. ...	16·3	57·0	9·1	5·5*	207	5 14

* Broke in fillet.   † Round notch 2 mm. diam.

TABLE LXI.

Effect of Copper on 25 per cent. Chromium Steel.

Carbon %	Chromium %	Copper %	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Izod Impact, ft. lbs.
0·26	23·6	nil	A.H. 950°C., W.Q. 700°C.	?	37·2	28·0	49·7	2 2 2
0·27	24·2	1·17	„ „	26·4	34·4	26·0	48·5	3 3 3
0·26	24·3	1·6	„ „	?	35·6	22·0	43·2	2 3 3
0·27	24·2	2·08	„ „	30·0	36·4	25·0	48·5	3 3 3
0·25	24·4	2·5	„ „	30·0	37·0	24·0	45·9	3 3 3

Here again the copper appears to have a slight hardening effect, but with a still higher chromium content this becomes negligible, even when as much as two or three per cent. of copper is present, as witness the tests in Table LXI.

(E) Chromium-Aluminium Steels.

Aluminium is not usually present, except in minute amounts, in stainless steel. Occasionally, however, it may be found in appreciable quantity, more particularly in low carbon material which has been made by some modification of the thermit process.

The effect of aluminium appears to be in many respects similar to that of silicon but in a much more pronounced degree. Like the latter element, aluminium raises very considerably the temperature of the Ac.1 point; it also
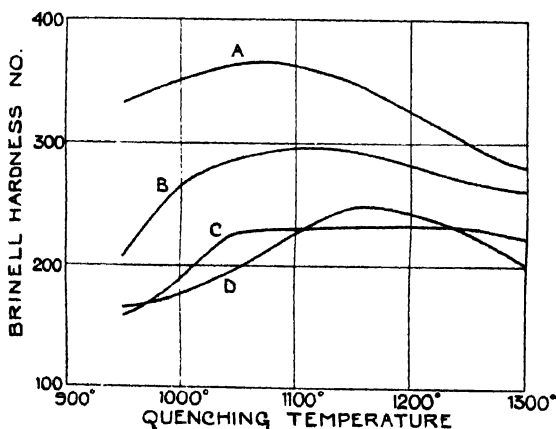
Fig. 143.   Effect of aluminium on the hardening of stainless iron :—

Curve	Carbon %	Chromium %	Aluminium %
A	0·09	12·0	0·15
B	0·11	13·3	0·49
C	0·11	10·9	1·08
D	0·11	12·0	1·46

raises the temperature of the A.3 change and lowers that of A.4, thus restricting the production of austenite. As a result, if present to the extent of about one per cent. or over, it may prevent low carbon material from hardening in any great degree even when water quenched in the form of small discs from any temperature up to at least 1,800°C. Such

a non-hardening iron would have advantages from some points of view; unfortunately, however, high aluminium material has a very low impact value, breaking under the impact test with a coarse crystalline fracture.
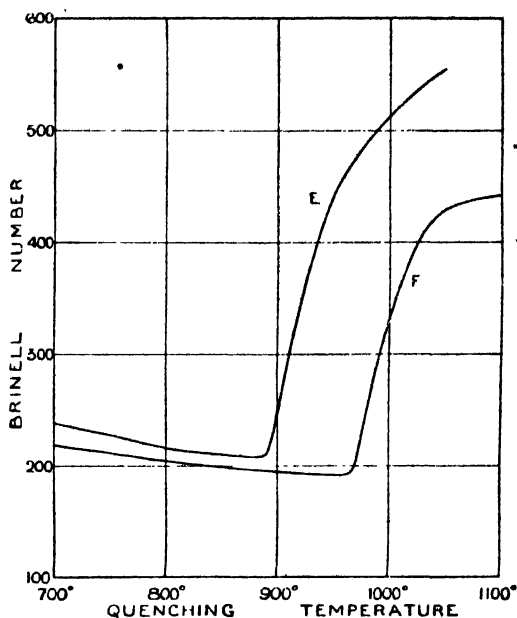
FIG. 144.   Effect of aluminium on the hardening of stainless steel :-

Curve	Carbon %	Silicon %	Chromium %	Nickel %	Aluminium %
E.	0·26	0·68	12·4	0·45	0·62
F.	0·26	0·67	12·2	0·45	1·13

The effect of aluminium on the hardening of stainless material is shown in Figs. 143 and 144.   In the former are plotted the Brinell hardness numbers obtained on quenching small discs, ¼ inch thick, of low carbon alloys, and a glance at these curves shows very plainly the effect of aluminium in raising the hardening temperature and also in preventing the metal hardening to any great extent.

Fig. 144 gives the figures obtained from two samples of higher carbon material.   The samples were in the form of bars ⅝ inch square and 2 inches long, and were quenched in water from the temperatures indicated.   These curves indicate, after allowing for the silicon and nickel in the steels,

that the presence of one per cent. aluminium raises the Ac.1 point about 120°C.

With regard to the impact value of these steels, samples E and F, when tested in the form of round bars, 1⅛ inches diameter, gave the following results :—

Steel.	Treatment.	Yield Point, tons per sq. in.	Max. Stress, tons per sq. in.	Elonga- tion per cent on 2 ins.	Reduc- tion of Area per cent	Brinell hardness Number.		Izod Impact, ft. lbs.
						After Hard- ening	After Temp- ering	
E.	A.H. 1,000° W.Q. 700° C. ...	46·0	56·0	16·0	47·2	337	248	18 23
F.	A.H. 1,050° W.Q. 700° C. ...	39·2	53·8	17·0	40·6	340	255	12 10 10

All the impact fractures were coarsely crystalline. The values for elongation and reduction of area in the tensile test are also not particularly good.

Similar impact results were obtained from the low carbon steels. Steel A (Fig. 143) when oil hardened from 1,000°C. and tempered at 700°C. (in the form of a round bar, 1 inch diameter) gave the following mechanical test :—

Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hardness Number		Izod Impact, ft. lbs.
				After Harden- ing.	After Tem- pering.	
85·2	42·6	30·0	67·8	321	207	104 105 102

a result typical of tough ductile material such as stainless iron should be. Samples B to D, on the other hand, when water hardened and tempered, in the form of ½ inch square bars, gave the values indicated below :—

Steel.	Treatment.	Brinell Hardness Number		Izod Impact, ft. lbs.
		After Hardening.	After Tempering.	
B.	W.H. 950° W.Q. 700° C.	212	166	12 14
B.	W.H. 1,050° W.Q. 700° C.	235	179	15 20
C.	W.H. 1,050° W.Q. 700° C.	207	174	10 11
D.	W.H. 1,050° W.Q. 700° C.	207	187	10 11

All the samples were coarsely crystalline, the coarseness being particularly evident in samples C and D, nor was it found possible to improve the appearance of the fractures by any treatment up to a temperature of 1,100°C.

(F) Chromium-Molybdenum Alloys.

The resistance of chromium-molybdenum alloys to chemical attack, particularly of acids, was noted by Borchers and Monnartz some years ago.   In 1910, they obtained a German patent (No. 246,015) in respect of alloys containing 10/60 per cent. chromium, together with 2/5 per cent. molybdenum, claiming for them high resistance to chemical action
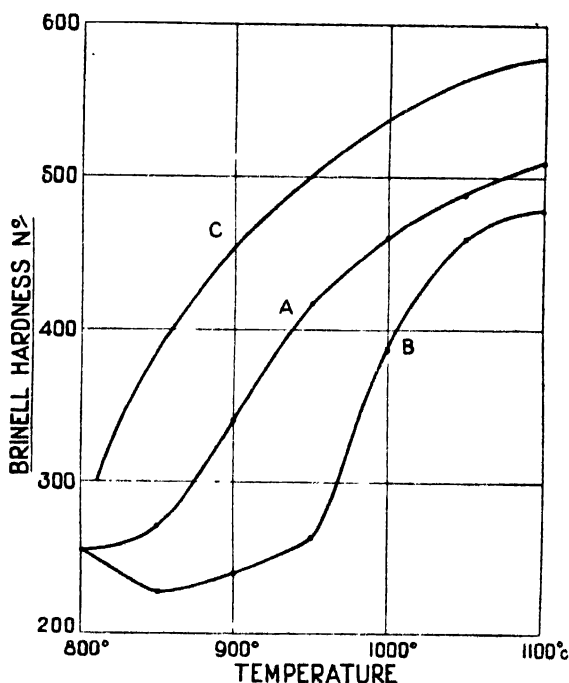
FIG. 145.   Brinell hardness numbers obtained from chromium-molybdenum steel containing 0·24% carbon, 12·8% chromium, 2·28% molybdenum after water quenching (Curve A) or air cooling (Curve B) from the temperatures indicated.   Curve C gives typical results obtainable on air cooling a steel free from molybdenum, but otherwise similar in analysis.

and mechanical workability.   The addition of one or two per cent. molybdenum to a chromium steel of the ordinary

stainless type has also a notable effect on the latter's resistance to mineral and organic acids, though the author is not aware that such steels are used commercially.

With regard to the effect of such a content of molybdenum on the mechanical properties of the steel, experiments indicate that the presence of this metal

(a) raises the temperature of the Ac.1 point.

(b) reduces to a distinct extent the air-hardening capacity of the steel, at least when cooled from the range of temperature of about one hundred degrees or so above the Ac.1 point.

These effects are apparent from the curves in Fig. 145 Curves A and B indicate the Brinell hardness numbers obtained from a steel containing 0·24 per cent. carbon 12·8 per cent. chromium, and 2·24 per cent. molybdenum. The figures plotted in curve A refer to small discs water quenched from the temperatures indicated while those in B were obtained from bars, one inch diameter, which had been air-cooled.   For comparison, curve C represents typical figures obtainable on air or oil hardening a steel free from molybdenum, but otherwise of similar composition.

Presuming, however, that a suitable hardening temperature is used for the molybdenum steel, the latter, when subsequently tempered, behaves very similarly to an ordinary stainless steel.   Probably the molybdenum steel is somewhat harder when fully-tempered than a steel free from this metal, but otherwise the presence of the molybdenum would appear to have little effect on the properties of the steel.   Thus a bar one inch in diameter of the steel referred to above, containing 2·24 per cent. molybdenum, 0·24 per cent. carbon, and 12·8 per cent. chromium, when oil-quenched from 950°C., and then tempered at 700°C., gave the following tests :—

Yield Point, tons per sq. inch.	Max. Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness No.		Izod Impact, ft. lbs.
				After Hardening.	After Tempering.	
34·0	49·6	27·0	59·3	332	235	47, 55, 46.

The yield point is somewhat low, an effect which may be attributed to the fact, indicated by the Brinell hardness

number, that the steel was not fully hardened by oil-quenching from 950°C. The maximum stress is also rather higher than would be obtained from an ordinary stainless steel of the same carbon content after similarly hardening and tempering (compare with results in Table VI, p. 106), but apart from this, the results are typical of ordinary stainless steel.

A similar conclusion would be drawn from the results of the following test on a stainless iron containing molybdenum :—

Carbon %	Chromium	Nickel	Molybdenum
0·08	13·2	0·80	0·97

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga-tion per cent. on 2 ins.	Reduc-tion of Area per cent.	Brinell Hardness No. Hard'd.	Temp'd.	Izod Impact, ft. lbs.
A.H.950°C., W.Q.700°	37·0	45·0	29·0	63·7	351	241	86 86 88

In addition to raising the temperature of the Ac.1 change, molybdenum, as has already been noted on page 68, decreases the range of existence of austenite by raising the
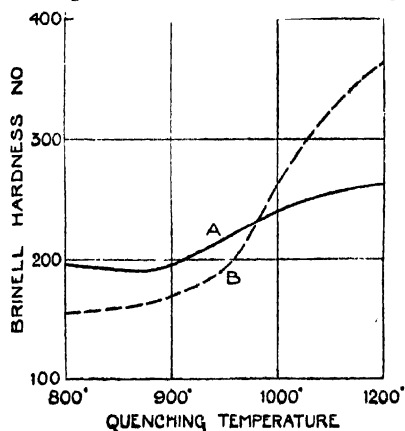
FIG. 146. Effect of molybdenum on the hardening of 17 per cent. chromium steel samples water quenched from temperatures indicated :—

Curve	Carbon %	Chromium %	Molybdenum %
A	0·21	17·2	2·33
B	0·17	17·1	nil.

temperature of A.3 and lowering that of A.4.   Behaving
thus in the same way as chromium, molybdenum does not
improve the hardening capacity or the mechanical properties
of the higher chromium steels.   For example, the curves in
Fig. 146 relate to steels containing 17·1/17·2 per cent.
chromium and they show that the one containing molybdenum
hardened less than the other, which was free from this metal,
and this in spite of the higher carbon content of the molyb-
denum steel.   The tests in Table LXII also indicate that
molybdenum has no beneficial effect on the mechanical
properties of such steels.

TABLE LXII.

Influence of Molybdenum on 17 per cent. Chromium Steel.

Mark	Carbon %	Chromium %	Nickel %	Molybdenum %
A	0·28	16·8	0·24	nil
B	0·28	17·1	0·20	1·01
C	0·21	17·2	0·26	2·33

Mark	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard'd.	Brinell Temp.d	Izod Impact, ft. lbs.
A	O.H. 950°C., W.Q.700°C.	30·0	42·0	27·0	58·2	311	207	38 37
B	A.H. 950°C., W.Q.650°C.	27·2	44·8	27·0	57·0	269	212	10 14
C	O.H. 1000°C., W.Q.700°C.	20·0	40·0	30·0	54·6	228	207	1 1

Patents* have been taken out by the Glockenstahlwerke,
A.G. for steels containing 0·1/1·2 per cent. carbon, 8/25 per
cent. chromium, 0·2/6·0 per cent. molybdenum and 0·5/2·0
per cent. nickel.   Up to 2·0 per cent. cobalt or 1·0 per cent.
titanium or aluminium may also be added.   It is claimed
that the steels are highly resistant to chemical action, possess
great strength and are capable of being hardened ; it is also
noted that the addition of the nickel renders the alloy more
ductile when hot.   It will be equally obvious, from the
data given in the previous pages, that the hardening capacity

of the alloys will depend on their nickel and carbon contents and that these will need to be about the maximum values specified if any appreciable hardening capacity is to be expected from steels in which the chromium and molybdenum contents approach 25 and 6 per cent. respectively.*

(G) Chromium-Tungsten Steels.

The effect of tungsten on tool steels is well known. Added to the extent of one or two per cent. to an ordinary carbon steel containing, e.g., one per cent. carbon, it improves the hardening capacity of the steel, raises somewhat the temperature required to harden it, and gives it a much finer fracture after similar conditions of heat treatment.   One
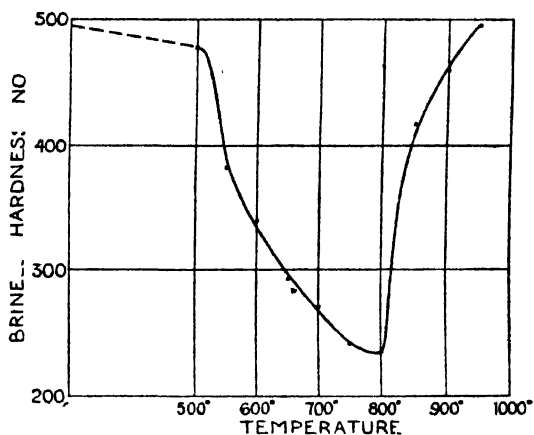
FIG. 147.   Effect of tungsten on the hardening and tempering of 12 per cent. chromium steel; samples previously A.H. 1,000° C., and then water quenched from the temperatures indicated :—

Carbon %	Chromium %	Tungsten %	Nickel %
0·32	11·6	1·40	0·25

might expect its effects on a hardenable stainless steel, for example, the ordinary " cutlery " quality, to be on the same general lines.   Actually, the addition of 1·4 per cent. tungsten to a " cutlery " quality stainless steel produced no noticeable effects on the steel's hardening and tempering characteristics, as may be seen by comparing Fig. 147 with curve A in Fig. 13.   When fully tempered, however, the tungsten steel is distinctly harder than the other.   This hardening effect is also noticeable in the tests quoted in

Table LXIII relating to steels containing about one half per cent. tungsten; the impact values of these steels are also particularly good.

TABLE LXIII.

Effect of Tungsten on the Mechanical Properties of 12/14 per cent.
Chromium Steel.

Carbon %	Chromium %	Nickel %	Tungsten %
0·30	12·6	0·44	0·55
0·29	13·3	0·58	0·50
0·25	13·0	0·62	0·43

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hardness No. Hard'd.	Temp'd.	Izod Impact, ft. lbs.
A.H.950°C. A.C.700°C.	40·0	54·0	23·0	54·6	460	241	48 55 50
A.H.900°C. A.C.700°C.	43·0	59·1	21·0	48·0	444	286	65 65 55
	40·3	51·6	24·5	58·2	387	241	61 56 60

Tungsten, however, has no similar beneficial effect on the properties of low carbon, high chromium steels, nor would such an effect be expected from its known action on the stability of γ-iron, to which reference was made on page 68. For example, the following results were obtained from a bar, one inch diameter, of steel containing 0·27 per cent. carbon 17·3 per cent. chromium, 0·20 per cent. nickel and 1·03 per cent. tungsten, after air hardening from 950°C. followed by tempering at 700°C.

    Brinell before tempering ... 228
      ,,   after   ,,   ... 207
    Izod Impact ...   . 15, 12, 12 ft. lbs.
    Fracture   ...   . Crystalline.

(H) Chromium-Cobalt Steels.

The similarity which exists in some respects between cobalt and nickel might lead one to expect that the effect of the former metal on high chromium steel would be broadly the same as that of the latter. Actually, however, cobalt,

appears to influence the properties of such steels to a much less degree than nickel.   For example, Fig. 148 shows the Brinell hardness numbers obtained on oil-quenched samples of
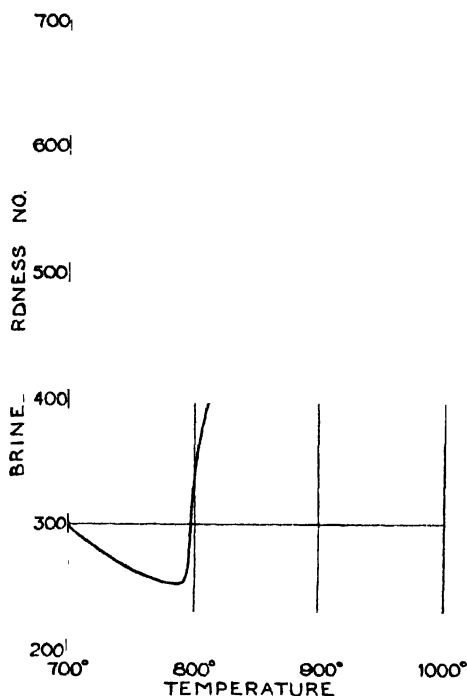
FIG. 148.   Relation between quenching temperature and hardness of steel containing :—

Carbon	Chromium	Nickel	Cobalt
%		%	%
0·43		0·30	2·45

a steel containing about 9 per cent. chromium and 2 per cent. cobalt ; the curve is not noticeably different from that given by a steel of similar chromium content but free from cobalt. The difference between cobalt and nickel may be observed by comparing this curve with curve 5 in Fig. 81 (page 138).

Possibly owing to its expense, cobalt does not appear to be used to any extent as a constituent of corrosion-resisting steels, except for one purpose.   High carbon, cobalt-chromium steels have been used for valves for internal combustion engines and are claimed to be superior to chromium steels for this purpose, though there seems to be

some doubt as to whether the claim is justified.*   A steel of this type, when hardened and then tempered at successively higher temperatures gave the hardness values indicated in Fig. 149.   The steel appears to retain its hardness somewhat better than a plain chromium steel after tempering at about 500°C. (*cf.* curve B, Fig. 83), but otherwise the curve is such as would be obtained from a steel free from cobalt but otherwise similar in analysis.   It may be noted that the Ac.1 point occurred at 803°C., indicating that cobalt has little or no effect on the position of this change point.
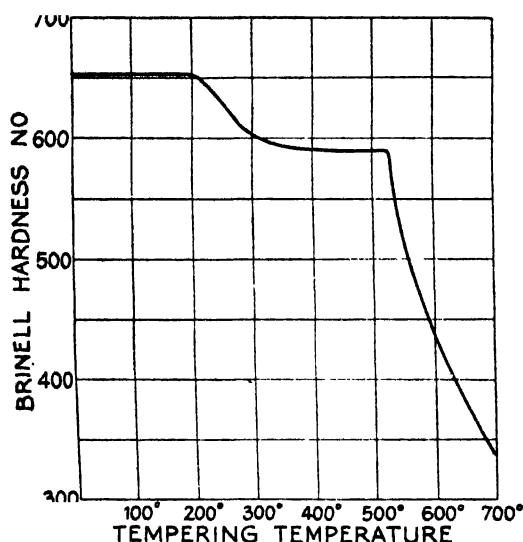
FIG. 149.   Relation between hardness and tempering temperature of valve steel containing :—

Carbon %	Chromium %	Cobalt %
1·42	13·0	3·64

(I) Free Cutting Stainless Steels.

The advent of the automatic lathe and the demand for the rapid production of machine parts, for which accuracy of form was at least of equal importance to mechanical properties, led to the production of "free-cutting" steels, which possessed the property of cutting cleanly and without tearing under machining conditions which would produce a

* See "Valve Steels for Internal Combustion Engines." L. Aitchison. *Proc. Inst. Auto. Eng.*, Vol. XIV (1919), p. 31.

rough, torn surface on a piece of ordinary mild steel. The earlier free-cutting steels (and some at least of those of more recent manufacture) had rather low impact values, but the technique of their production has progressed during the last few years so that in addition to having these desirable machining characteristics they may also possess very satisfactory mechanical properties (particularly with regard to toughness as measured by the Izod impact test) such as make them suitable, for example, for case-hardened articles subject to shocks.

There are probably many engineering applications where a stainless steel possessing machining qualities of the " free-cutting " type would be valuable. The ordinary stainless irons, which possess suitable mechanical properties, do not always machine well; they are liable to tear, for instance, in screw cutting. This is especially the case if they have been annealed so as to produce a very soft material; they are much better when hardened and tempered. In many instances, the requisite machining ability may be secured by using a material with a rather higher carbon content, e.g., 0·15 or 0·2 per cent. in the hardened and tempered condition. Although somewhat harder than the stainless irons—it will have a tensile strength of about 45 tons per square inch—material so treated machines more cleanly than the very soft varieties. It should also be noted that the higher chromium irons, which do not harden appreciably when quenched from 950°C., or thereabouts, frequently machine distinctly better in this quenched condition than when annealed. At the same time, they are decidedly more brittle when so treated and unless accuracy of form is the only desideratum, they should be tempered after machining in this condition and before being put into service.

Efforts have been made, however, in the United States to produce a free-cutting stainless iron similar to the ordinary free-cutting steel, so widely used for automatic machine work, as regards its machining qualities but possessing the desirable property of resistance to corrosion. A prominent feature of the ordinary carbon steel product is its relatively high sulphur content—generally 0·1/0·15 per cent.—and experiments carried out by F. R. Palmer* showed that a similar, or somewhat greater, sulphur content notably

* *Trans. A.S.S.T.*, December, 1928, p. 877.

improved the machining qualities of ordinary 14 per cent. chromium stainless iron. The presence of about 0·15 per cent. sulphur, however, introduced another difficulty, red-shortness, and it was deemed inadvisable to add manganese to counteract this—the method employed in all ordinary steels—as it was thought that the presence of this metal reduced the resistance of the iron to general corrosion, though the author is not aware of evidence on which such an opinion could be based. As an alternative, zirconium was tried and it is claimed that an addition of this metal as a sulphide, and to the extent of 0·4 per cent. of this compound, improves the machining qualities considerably and at the same time produces no ill effects on mechanical properties or resistance to corrosion.

It may be mentioned that A. L. Field[*] investigated, in 1924, the effect of zirconium on the hot rolling properties of ordinary steels containing 0·075/0·32 per cent. sulphur, and found that the zirconium reacted quantitatively with the sulphur in the steel to form zirconium sulphide (ZrS_2), no excess of the reacting metal being necessary as is the case with manganese. Like manganese sulphide, zirconium sulphide is plastic at rolling temperatures and hence does not interfere with the hot working of the steel. It is visible in the microstructure as grey inclusions, elongated by the mechanical treatment received by the metal.

TABLE LXIV.

Mechanical Properties of Zirconium-Treated Stainless Iron.
Sample (1) Stainless Iron
  ,, (2) ,, ,, + 0·4 per cent. Zirconium Sulphide.

TREATMENT. Hardened, then	Sample	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of area per cent.	Brinell Hardness No.	Izod Impact, ft. lbs.
Tempered 700°F. ...	(1)	56·2	69·4	17·2	55·2	341	36
	(2)	57·2	73·0	13·7	35·3	348	32
,, 1100°F. ...	(1)	44·4	51·8	22·1	71·7	228	82
	(2)	42·0	50·5	17·7	52·4	241	42
,, 1425°F. ...	(1)	30·3	39·3	30·8	73·2	170	96
	(2)	29·0	39·1	25·5	59·3	170	87

[*] *Trans. A.I. Min. & Met. Eng.*, February, 1924.

As regards the mechanical properties of the zirconium-treated stainless irons, the figures in Table LXIV relating to material containing about 14 per cent. chromium, are quoted from the paper by F. R. Palmer. The figures indicate that the zirconium-treated material is somewhat less tough and ductile than the other, but the difference would not be of any serious moment for many purposes.

This specially treated iron is a product of the United States ; so far as the author is aware, it has not been used in this country.

INFLUENCE OF VARYING TREATMENT AND COMPOSITION ON THE RESISTANCE TO CORROSION OF STAINLESS STEELS

CHAPTER V

The subject of the corrosion of iron and its alloys is extremely complex; a great deal of experimental work has been carried out, there are numerous papers bearing on the subject to be found in scientific and technical literature and several the ries have been propounded to explain the experimental results, often of an apparently contradictory nature, which have been obtained by various workers. Until quite recently, the two most important theories with respect to the corrosion of iron were the " acid " and " electro-chemical " theories. The former theory regarded the presence of, at least a minute proportion of, some acid as necessary in order that corrosion could take place whereas the latter held that the small physical and chemical variations present in samples of even the purest metals obtainable set up electro-chemical effects which would cause corrosion to take place in the absence of any free acids. Neither theory satisfactorily explained all the phenomena of the corrosion of iron, however, and hence special theories have been developed during recent years to account for the observed results. Some of these theories depend on chemical attributes of iron which are not possessed by other metals and, as they obviously do not apply to these, they tend to complicate matters.

Investigations carried out recently by U. R. Evans,* following on the work of Aston,† have served, however, to reconcile some of the conflicting statements and evolve some order in the theories of corrosion. According to

* Evans : *J. Inst. Metals*, Vol. 30, p. 239. *Trans. Faraday Society*, Vol. 18, p. 1 ; Vol. 19, pp. 201 and 789 ; *J.S.C.I.*, Vol. XLVI (1927), pp. 347, 363 ; Vol. XLVII (1928), pp. 55, 62, 73 ; *J.C.S.*, 1927, p. 1020 ; 1929, pp. 92, 111, 2651 ; 1930, p. 1361 ; and other papers. See also the book, " The Corrosion of Metals," by the same author.

† J. Aston : *Trans. Amer. Electro-chem. Soc.*, Vol. 29 (1916), p. 449.

Evans, corrosion is electrochemical in character, but his theory differs from the older one in that he believes the potential differences set up in different parts of a sample, which cause the corrosion, are due not only to variations in the metal itself but also in the corroding fluid surrounding it. The effect of variations in the fluid may be illustrated by the action of the small amount of dissolved oxygen which is always present in ordinary water. If a sample of ordinary steel sheet is immersed in a large tank of water, the amount of dissolved oxygen which the water contains will very probably soon vary from place to place in the tank, even though the water was well mixed at first. Evans' work has shown conclusively that, in such a case, electro-chemical action is set up as a result of this difference in oxygen concentration and that when this happens, the part of the steel sheet in contact with the water containing least oxygen in solution acts as the anode and is, therefore, attacked at a faster rate than the part bathed by the water with high oxygen content, which functions as cathode. This result is extremely important as it offers the first convincing explanation of the known fact that excessive corrosion is often produced at places where oxygen has the least access, such places, for example, as pits or grooves, or under dirt or debris, including products of corrosion, which may have settled on part of the surface of the metal. It may also be the cause of the tendency which stainless steel has been observed to possess of undergoing corrosion at the point where it is supported when immersed in some fluids.

The author has no desire, however, to enter into a detailed discussion of the present state of the theories of corrosion ; it would be outside the scope of this book.* Suffice it to say that though much headway has been made, notably as a result of the work of Evans, Friend, Bengough, Vernon and others, very much remains to be elucidated. Before considering the particular problem of the resistance to corrosion of stainless steel, it may be well, however, to consider briefly one or two fundamental facts with regard to the corrosion of iron.

* To those interested, the author would especially recommend a study of " The Corrosion of Metals," by U. R. Evans (Arnold, London, 2nd Edition, 1926). The experimental work of Dr. Friend, mainly published in the *Journal of the Iron and Steel Institute*, should also be consulted.

Whether a sample of absolutely pure iron, which was physically uniform in every part, would corrode if immersed in absolutely pure water may be a matter of doubt ; there can be no doubt, however, that the purest iron commercially available will corrode in ordinary distilled water or in ordinary drinking water. There is also no doubt that, on corrosion taking place, the iron goes into solution in the water and is subsequently precipitated from this solution as a hydroxide, either at or near the spot where it dissolved or after diffusing an appreciable distance through the water. Secondly, the less homogeneous, either physically or chemically or both, a sample of iron is, the greater, as a general rule, is its tendency to corrode. Thus the addition of carbon to iron produces a carbide which may exist as separate particles more or less unevenly distributed through the mass of the metal. This carbide of iron is electronegative to iron and hence tends to increase the rate of corrosion of the latter. A study of the microstructure of ordinary steels shows that these, under different conditions of heat treatment, may be either homogeneous or heterogeneous and this to a varying degree. Their rate of corrosion under such differing conditions also varies.

It is probable that the question of heterogeneity—either chemical or physical—is of even greater importance in corrosion resisting steels than in ordinary irons and steels. Normally, the latter corrode relatively rapidly in whatever structural condition they may be ; varying degrees of heterogeneity may therefore alter to some extent the rate at which they are attacked but will not determine whether corrosion occurs or not. On the other hand, the presence of heterogeneity in corrosion resisting steels may lead to them being attacked under conditions which they would resist completely if they were structurally homogeneous. The effects produced by heterogeneity are therefore likely to be more spectacular in the corrosion resisting steels than in the others.

One may draw a comparison, in this respect, between the cast and forged (or rolled) conditions of a given corrosion resisting steel. It has already been pointed out that, owing to selective freezing, all types of these steels possess a certain degree of heterogeneity in the cast condition, and that this is reduced in amount during hot working operations. It is probable that the greater local differences in composition

found in the cast condition, as compared with the hot worked form, of any stainless steel, are partly responsible for the undoubtedly greater degree of resistance to corrosion possessed by the latter form. In this respect, some of the austenitic alloys 'would appear to have some advantage over the hardenable forms of stainless steel because, in the form of castings, they do not exhibit such, marked structural unevenness, after suitable heat treatment, as do the latter types of steel.

Applying these two fundamental ideas to the special problem of stainless material, it is evident in the first place that the presence of sufficient chromium in solid solution in iron reduces the solubility of this metal in water practically to zero. It is not known why the addition of suitable amounts of chromium to iron should have this effect ; it seems probable however, that it is due largely to what is known as " passivity." It is common knowledge that iron or ordinary steel is readily attacked by nitric acid so long as the strength of the acid does not exceed that corresponding to a specific gravity of about 1·25. Somewhat stronger acid than this, e.g., corresponding to a specific gravity of 1·3 or 1·35, attacks these metals when they are first immersed in the acid, but after an interval, the rate of attack falls off markedly and may cease altogether. With still stronger acid, e.g., the concentrated form as ordinarily sold and having a specific gravity of 1·42, no attack appears to take place at all, or as it is generally said, in such an acid the metal becomes " passive." Iron which has been made passive by the action of strong nitric acid retains, for a longer or shorter period after being taken out of the acid, certain peculiarities in its behaviour to other reagents. Thus it is not immediately attacked by nitric acid of specific gravity 1·20 nor will it precipitate · copper from solutions of some salts of this metal in the manner that iron does normally. In other words, the passive iron has a greater resistance to the attack of certain chemicals than has the normal metal. Such a passive condition may be produced in iron by the action of other reagents, generally of an oxidising nature, or by electrochemical means. The passivity produced in iron by any such means is more or less transient ; although the passive metal resists · for a short period other reagents, which do not themselves produce passivity in the metal, such resistance is only

temporary and at the end of a longer or shorter time, the metal is attacked.

Until recently, the cause of passivity was not definitely known, though it appeared to be extremely probable that the surface of a passive metal was covered with a layer, possibly only a few molecules thick, of an oxide of the metal, further action being prevented by this film.   In 1927,[*] however, U. R. Evans set all doubts at rest by actually isolating the thin film of oxide from passive forms of pure iron and of mild steel.[†]   He showed that films are formed on the surfaces of these metals even on exposure to the atmosphere for a short time and that such films consist of ferric oxide and are not more than about 0·000002 inches (0·00005 m.m.) thick.   Being so thin and in optical contact with a highly reflecting metal surface, they are not visible ; but they can be isolated by dissolving the metal from underneath them and are then easily seen, handled and identified as iron oxide.   If iron is heated, the thickness of the surface film increases ; when it reaches suitable values, it sets up interference effects between the light reflected from the front of the film and that from the metal underneath and thus gives rise to the well-known temper colours.   Evans also found that the oxide layer produced on pure electrolytic iron offered a greater degree of protection to that metal than did the film produced under similar conditions on mild steel. It is very probable that the relative inefficiency of the latter film is due to the presence of carbide in the mild steel ; it seems likely that the carbide interferes with the continuity of the oxide layer and also, being electronegative to the ferrite, causes the latter to be electrochemically attacked, thus leading to the protective film being undermined.

The metal chromium exhibits passivity effects in a much more pronounced manner than iron ; in the passive condition, it behaves in several respects like a " noble " metal.   It seems probable that when chromium is added to iron, it increases the stability of the oxide film so that the latter gives much greater protection to the metal underneath ; in other words, it greatly increases the tendency to passivity already present in the iron.

[*] " The Passivity of Metals." Part I.   *J.C.S.*, May, 1927, p. 1020.

[†] He has since isolated the films on stainless steels, see " The Passivity of Metals," Pt. III.   *J.C.S.*, November, 1929, p. 2651.

Evans also showed that although a certain degree of passivity was produced in electrolytic iron and mild steel by merely exposing their surfaces to the atmosphere for some time (he actually isolated the oxide films so produced) the effectiveness of the protecive film of oxide was much greater if it was produced under more strongly oxidising conditions, e.g., by immersion in strong nitric acid or a solution of potassium chromate. If the resistance of high chromium steels to general corrosion is due to a similar film, produced practically instantaneously on a freshly prepared metallic surface by exposure to air, it is likely that a still more protective film would be produced on the surface of these metals by exposing them to strongly oxidising conditions, e.g., to strong nitric acid. There is distinct evidence that this is the case. The ordinary " cutlery " type of stainless steel (0·8 per cent. carbon, 12/14 per cent. chromium) is attacked quite rapidly by dilute sulphuric acid ; placing a sample in a 10 or 20 per cent. solution of this acid leads to the immediate attack of the metal and the formation of bubbles of hydrogen. If, however, the sample be placed in strong nitric acid for some time (this acid having apparently no action on the metal) and then, after thorough washing, placed in the dilute sulphuric acid, the latter will have no immediate attack on the metal. Actually, in such a test, the sulphuric acid produced no visible effect on the steel for about six or seven minutes ; after this there was a slow action but the normal rate of attack was not reached until the sample had been immersed in the acid for about three hours.

A still more striking result may be obtained with the austenitic chromium-nickel steels. " Anka " steel, for example, is normally very slowly attacked by 10 per cent. sulphuric acid ; if, however, a piece of " Anka " be placed in nitric acid for some time, it may then be transferred to 10 per cent. sulphuric acid and be kept therein for days without any action being produced. Fig. 150 illustrates this. It represents the appearance of two samples of " Anka" steel after 8 days in 10 per cent. sulphuric acid ; sample A was polished and then placed immediately in the acid ; sample B was immersed for 18 hours in 80 per cent. nitric acid after polishing and before placing in the sulphuric acid. The production of marked passivity effects in this manner

Plate XXVII

B **A**
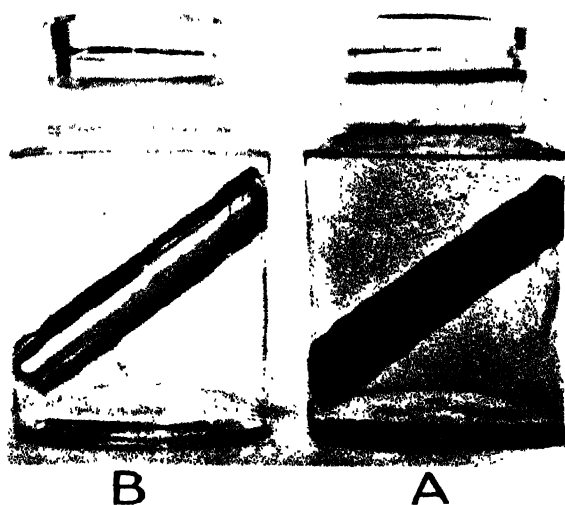
Fig. 150   Passivity effects produced by nitric acid.   Samples of Anka steel (15/16 per cent. chromium, 10-11 per cent. nickel, 0-1 per cent. carbon) after 3 days immersion in 10 per cent. sulphuric acid.

Sample ' A,' placed in the acid immediately after polishing

Sample ' B,' immersed for 30 hours in 30 per cent. nitric acid after polishing and before placing in the sulphuric acid

needs to be kept well in mind by those carrying out corrosion tests on these steels.*

When chromium is added in small quantities to steel, it appears at first to be entirely associated with the carbon in the latter. As more chromium is added, the demands of the carbon in this respect become satisfied and the balance of the chromium then goes into the solution in the iron. Obviously, therefore, in steel of any given chromium content, the amount of chromium actually in solution in the iron itself will depend on the amount of carbon in the steel.

The composition of the carbides in chromium steels has been the subject of a number of researches and perfect agreement does not exist between the results obtained by different investigators. It is not certain whether the carbide has a constant composition, there being evidence to show that the ratio of iron, carbon and chromium in it may vary to some extent under different conditions of heat treatment. Some of the earlier determinations had reference to steels containing much larger amounts of carbon than are normally present in stainless steels and it is possible that the carbide in such steels may not be identical with that found in those of lower carbon content. The most recent determinations are those by B. Kalling† who states that the carbide in steels containing 13/30 per cent. chromium has the same composition, this being approximately 5·3/5·4 per cent. carbon and about 63 per cent. chromium. On this basis, it may be taken that the ratio of chromium to carbon in the carbide is about 12 to 1.‡

The chromium which exists as discrete particles of carbide is obviously not useful in increasing the resistance to corrosion of the ferrite in which it is embedded, though its presence may be necessary on the score of requisite mechanical properties. The added chromium only becomes of value in promoting corrosion resistance when it is actually dissolved in the iron. It is obvious, therefore, that the amount of carbon present in the steel has a very decided influence on the amount of chromium available for inducing resistance to corrosion in the iron and also that the physical condition of

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* See also page 313.

† *Jernkont. Ann.*, 1927, p. 609.

‡ Bain and Aborn suggest that the chromium content of the carbide may be much higher, between 75 and 90 per cent.; in which case, the ratio of chromium to carbon in the carbide would be between 15 : 1 and 19 : 1.

the carbide present in any one steel will affect the degree of resistance to corrosion of that steel.   In this chapter it is intended to indicate firstly, how the degree of resistance in any one sample of stainless steel is affected by variations in the heat treatment to which it may be subjected and, secondly, the general effect of alterations in composition on the resistance to corrosion of stainless steels.

(1) EFFECTS OF HEAT TREATMENT ON RESISTANCE TO CORROSION.

From the general principle that heterogeneity tends to increase the rate of attack of steel by different corroding media, we should expect to find, and actually do find, that the greatest resistance to corrosion of any one steel is obtained after treating it in such a manner that it consists entirely of one constituent, while the least resistant form is obtained on annealing the steel so as to produce a complete separation of the carbide it contains.   In the former case, all the chromium (as well as the carbon) is in solution in the iron and therefore the full effect of the whole of the chromium present is obtained ; in the latter case, not only does the separation of carbide tend to decrease the resistance to corrosion owing to galvanic effects but, in addition, it lowers the concentration of the chromium in solution in the iron and impairs the continuity of the protective oxide skin which, it seems probable, forms on the surface of the steel.   All these effects tend to make the steel less resistant to corrosion than when it contained the whole of its chromium in solution.

The structural conditions produced by heat treatment operations in hardenable and in austenitic steels being so radically different, it will be convenient to consider each group separately in an attempt to assess the influence of heat treatment operations on corrosion resistance.

(a) Hardenable Steels.

As the structural effects produced by different heat treatment operations are concerned largely with the mode of existence of the carbide in the steel, it is likely that the effects of these treatments on corrosion resistance will be greater the higher the carbon content of the steel.   On the other hand, with equal amounts of carbon, an increase in chromium content is likely to reduce the effect of varying

treatment on corrosion resistance because the higher the
total chromium content, the smaller the fraction of it which
is affected, as regards mode of existence, by the solution or
precipitation of a given amount of carbide in the steel.   An
ordinary " cutlery " quality stainless steel, containing about
0·3 per cent. carbon and 12/14 per cent. chromium, may
therefore be selected as being likely to show the effects
of different heat treatment processes in a more marked
manner than other stainless steels or irons containing
more chromium or less carbon or both.   The effects on
such a steel will therefore be first noted and then the
differences likely to be found in material of other
compositions.

HARDENING.   The greatest resistance to corrosion will
be obtained by quenching the steel from a temperature
sufficiently high to dissolve all the carbide which it contains :
in the case of the ordinary " cutlery " type of steel, this
temperature is about 1000°/1050°C.   In practice, however,
it is found that quenching a steel of this type from a tem-
perature of 900°/950°C. produces a material which is
practically insoluble in water and certain other media, such
as vinegar and fruit juices, and that increasing the hardening
temperature beyond this range produces no marked improve-
ment while, on the other hand, it seriously increases the risk
of cracking during hardening.   In the case of samples which
have subsequently to be tempered almost completely there
would appear to be no advantage whatever, from the point
of view of resistance to corrosion, in raising the quenching
temperature sufficiently high to take into solution the
remnants of the carbide left undissolved at 900/950°C.,
because the whole of the dissolved carbide will be thrown
out of solution again in the subsequent tempering operation.*
In this case, the quenching temperature should be selected
to give the best mechanical properties, in the manner described
in the previous chapters.

The effect of raising the quenching temperature on the
resistance to corrosion of quenched samples may, however,
be illustrated by using steels with a lower chromium content
than that present in stainless steels, the former being more
susceptible than the latter to the influence of heat treatment.

* The salt spray tests quoted on p. 266, suggest that quenching from a very
high temperature may lessen the resistance of subsequently tempered samples.

For example, samples of steel which had the following
analysis : --

Carbon   ... 0.53%
Silicon   ... 0.73%
Manganese   ... 0.21%
Chromium   ... 8.60%

and was, therefore, considerably outside the range of composi-
tion generally used for stainless material, were quenched from
the following temperatures :—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Temperature ...	950° C.	1,000° C.	1,050° C.	1,120° C.	1,200° C

After quenching, No. 1 contained a considerable amount of
free carbide, No. 2 less, No. 3 only traces, whilst Nos. 4 and 5
consisted entirely of martensite.   The pieces were ground
and polished, and then tested by placing a small drop of
vinegar on each polished surface and allowing it to dry
gradually.*   The dry residues from the drops were then
washed off in water.   Sample No. 1 was then found to be
decidedly stained by this test, No. 2 less so, No. 3 only
slightly, while Nos. 4 and 5 were unattacked.   This indicates
very clearly that the resistance of the material to staining
increases with the quenching temperature and with the
progressive solution of the carbide which takes place as the
temperature rises.

TEMPERING.   From the fact that no appreciable loss of
hardness is produced on tempering hardened samples of
stainless steel up to about 500°C., and that after such
tempering the structure of a previously quenched sample is
still martensitic, it would not be expected that such a tem-
pering would have any great effect on the resistance to
corrosion of the hardened material, nor has any such effect
been found.   This fact is of great importance commercially,
as tempering in this way removes to a very great extent the
internal stresses set up during hardening and also improves
considerably the ductility and toughness of the material,
as was shown in the last chapter.

* This spot test with vinegar is regularly used in testing material for cutlery.
It is a more severe test than placing the sample for 12 or 24 hours in vinegar.

The sudden and marked fall in hardness which is produced as the tempering temperature rises from 500° to 600°C., is accompanied by a lessened resistance to corrosion of the material. Such softened material, for example, may stain when tested with vinegar as described earlier, but. even in this condition it is attacked extremely slowly. Whether it will actually stain or not with the vinegar test depends on the amount of carbon and chromium it contains. As probably the greater part, if not all, of the carbide is thrown out of solution by tempering at 550°/600°C. and the chief effect of tempering at higher temperatures than this consists in the coalescence of the small carbide particles already present into others larger in size, it would not be expected that there would be any marked difference in the resistance to corrosion of samples tempered at 600°C. and of those tempered at higher temperatures, e.g., 700°/750°C. On theoretical grounds there are probably two opposing effects produced by the higher tempering range :—

(a) A further small precipitation of carbide resulting in a diminution of the concentration of dissolved chromium and hence tending to produce a lessened resistance to attack.

(b) The coalescence of the carbide particles causes a very decided decrease in the total surface area of the latter. It is reasonable to suppose that this diminution of surface will tend to reduce any galvanic effect between the carbide and the ferrite and hence tend to increase the resistance to attack.

It is quite possible that these opposing effects may have different relative values with different corroding media. In almost all cases, however, it is found that resistance to corrosion reaches a minimum in material tempered at 550°/600°C., and that higher tempering temperatures than this give a greater surface stability.

The effect may readily be shown by testing a sample of " cutlery " steel containing, preferably, rather less chromium than usual. For example. samples of steel containing 0·34 per cent. carbon and 11·6 per cent. chromium, which had been hardened and then tempered at various temperatures, were placed for 21 days in malt vinegar. At the end of that period, the pieces which had been tempered at temperatures up to 500°C. showed no signs of attack. Those

tempered at 550° and 600°C. had been slightly but distinctly
attacked, producing an etched appearance on their polished
surfaces.   The losses in weight were 0·0026 and 0·0019
grams per square cm. of surface respectively.   The sample
tempered at 700°C. was obviously less attacked ; the etching
effect was less marked and the loss in weight was only one
half to one-third of the preceding figures, viz., 0·0008 grams
per square cm.

A similar maximum rate of attack in samples tempered
at 550°/600°C. is also generally noted when dilute solutions
of organic and inorganic acids are the corroding reagents,
as may be seen from the results quoted in Table LXV.

<div align="center">

TABLE LXV.

Effect of Tempering on Rate of Acid Attack.

(Rates of attack in grams per sq. m. per hour.)

</div>

Carbon %	Chromium %	Nickel %
0·30	12·6	0·79

Acid.	Tempering Temperature.			
	500°C.	550°C	600°C.	700°C.
5% Acetic Acid	nil	0·77	0·41	0·21
10% Citric Acid	nil	0·95	0·40	0·14
10% Formic Acid	4·71	3·67	0·99	0·72
N/10 Nitric Acid	1·29	4·23	3·54	2·47
25% Phosphoric Acid	0·13	2·7	8·06	4·18
5% Sulphuric Acid	29·4	38·5	30·1	26·9
5% Tartaric Acid	0·02	1·02	0·47	0·19

Results of a similar nature are also obtained when other
corroding agencies than dilute acids are employed.   Thus
in a comprehensive series of tests on the corrosive effect of
salt water spray on various steels, Strauss and Talley[*]
found that the curves connecting tempering temperature and
loss in weight, during tests lasting a month and in which
the samples were actually subjected to the spray for 500 hours,
showed a distinct maximum at about 600°C.   The curves in
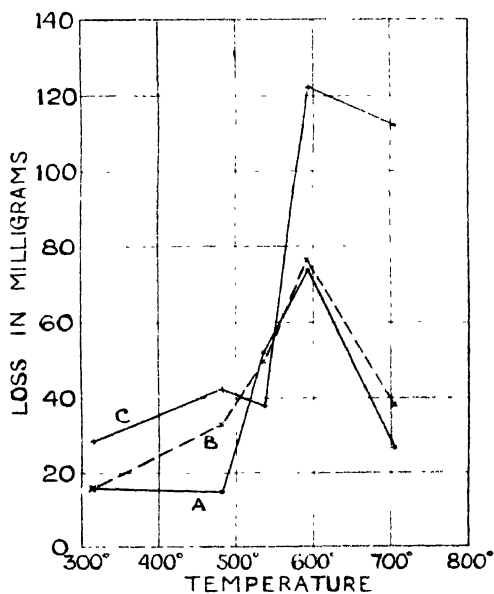
[*] *Proc. A.S.T.M.*, Vol. 24, Pt. 2, 1924.

Fig. 151.   Effect of tempering on resistance to salt spray.   Carbon 0·37 per cent. ;   chromium 14·5 per cent. ;   nickel nil.

Samples oil hardened and then tempered at the temperatures indicated.

Curve		Hardening Temperature.
A	...	925° C.
B	...	1040° C.
C	...	1150° C.
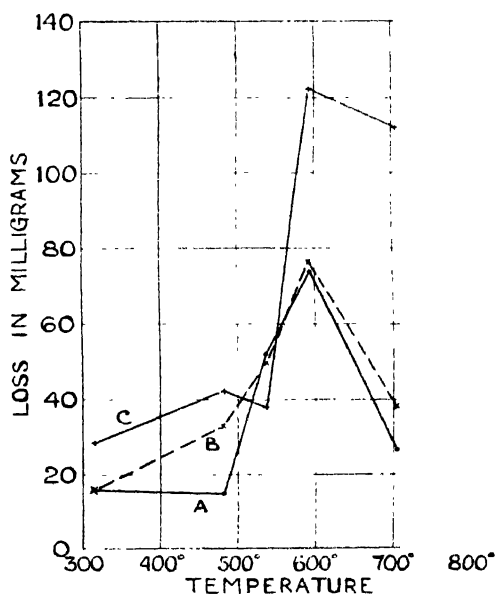
Fig. 152.   Effect of tempering on resistance to salt spray.   Carbon 0·8 per cent. ;   chromium 18·16 per cent. ;   nickel 0·24 per cent.

Samples oil hardened and then tempered at the temperatures indicated.

Curve			Hardening Temperature.
A	...	...	925° C.
B	...	...	1,040° C.
C	...	...	1,150° C.

tempered at 550° and 600°C. had been slightly but distinctly attacked, producing an etched appearance on their polished surfaces. The losses in weight were 0·0026 and 0·0019 grams per square cm. of surface respectively. The sample tempered at 700°C. was obviously less attacked ; the etching effect was less marked and the loss in weight was only one half to one-third of the preceding figures, viz., 0·0008 grams per square cm.

A similar maximum rate of attack in samples tempered at 550°/600°C. is also generally noted when dilute solutions of organic and inorganic acids are the corroding reagents, as may be seen from the results quoted in Table LXV.

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Acid.	Tempering Temperature.			
	500°C.	550°C.	600°C.	700°C.
5% Acetic Acid ...	nil	0·77	0·41	0·21
10% Citric Acid ...	nil	0·95	0·40	0·14
10% Formic Acid ...	1·71	3·67	0·99	0·72
N/10 Nitric Acid ...	1·29	4·23	3·54	2·47
25% Phosphoric Acid ...	0·13	2·7	8·06	4·18
5% Sulphuric Acid ...	29·4	38·5	30·1	26·9
5% Tartaric Acid ...	0·02	1·02	0·47	0·19

Results of a similar nature are also obtained when other corroding agencies than dilute acids are employed. Thus in a comprehensive series of tests on the corrosive effect of salt water spray on various steels, Strauss and Talley[*] found that the curves connecting tempering temperature and loss in weight, during tests lasting a month and in which the samples were actually subjected to the spray for 500 hours, showed a distinct maximum at about 600°C. The curves in

[*] *Proc. A.S.T.M.*, Vol. 24, Pt. 2, 1924.

Fig. 151. Effect of tempering on resistance to salt spray. Carbon 0·37 per cent.; chromium 11·5 per cent.; nickel nil.

Samples oil hardened and then tempered at the temperatures indicated.

Curve	Hardening Temperature.
A	925° C.
B	1040° C.
C	1150° C.

Fig. 152. Effect of tempering on resistance to salt spray. Carbon 0·8 per cent.; chromium 18·16 per cent.; nickel 0·24 per cent.

Samples oil hardened and then tempered at the temperatures indicated.

Curve	Hardening Temperature.
A	925° C.
B	1,040° C.
C	1,150° C.

Fig. 151 relate to a steel of typical " cutlery " composition and, besides exhibiting this characteristic, they suggest that a very high hardening temperature is not an advantage from a corrosion resistance point of view ; it is equally undesirable mechanically.   Similar characteristics are visible in Fig. 152 which is also interesting in that it shows, by comparison with Fig. 151, that any beneficial effect of an increase of about 4 per cent. in the chromium content of the steel is more than balanced by raising the carbon from 0·37 to 0·80 per cent.

Complete immersion in sea water for 52 weeks produced losses in weight of a " cutlery " quality steel as indicated by curve A in Fig. 153.   In this case, there is again a well
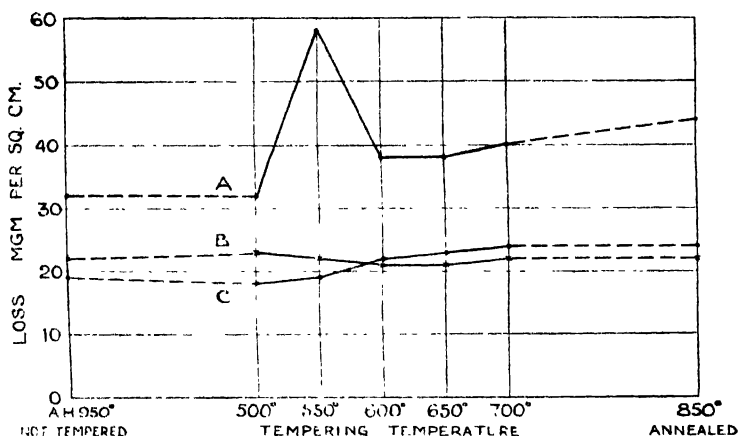
FIG. 153.   Effect of heat treatment on resistance to sea water.

Curve	Carbon	Chromium	Nickel
	/o	/o	/o
A	0·30	12·6	0·78
B	0·20	17·4	2·19
C	0·09	17·9	2·08

defined maximum but at a rather lower temperature than in the salt spray tests quoted above.   Curves B and C in this diagram show that the effects of different heat treatment conditions become much less if the chromium content be raised considerably, the carbon remaining about the same. The two steels referred to here gave losses of the same order of magnitude whether hardened, hardened and tempered, or annealed.   The same effect is shown in Fig. 154, reproduced

from the paper by Strauss and Talley and relating to salt spray tests carried out in the same manner as those recorded in Figs. 151 and 152.
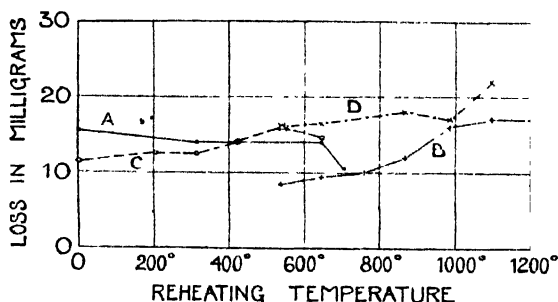
Fig. 154.   Effect of heat treatment on resistance to salt spray :—

'urve	Carbon %	Chromium %	Nickel %	Treatment.
A	0·18	15·84	0·08	W.H. 980° C., tempered as indicated.
B		,,	,,	Quenched as indicated.
C	0·19	16·5	0·34	W.H. 980° C., tempered as indicated.
D	0·09	15·96	0·64	Quenched as indicated.

From a consideration of all these diagrams, it would ppear that tempering in the range 550°/600°C. is less ·sirable, from a corrosion resistance point of view, than at ny other temperature but that the differences are not likely ·· be very noticeable in stainless irons containing about ·1 per cent. or more chromium or in steels with 0·2/0·3 per ·nt. carbon when the chromium is not less than about ·6 per cent.   Fortunately the range 550°/600°C. is also the ·ast desirable from a mechanical point of view because, as ·s already been mentioned, the hardness of the steel falls ·· rapidly as the tempering temperatures rises from ·0° to 600°C. that it is difficult to secure prescribed roperties by tempering in this range.

It will be noted that Strauss and Talley obtained ·aximum rate of attack at 593°C. while in the author's ·urves, Fig. 153, an equally well defined maximum is evident ·· 550°C.   An explanation can be found for this apparent ·screpancy.   The rapid fall in hardness referred to above ·tually commences at a temperature just below 550°C. ·he samples tempered by the American investigators at 538°C. (1000°F.) had not quite reached this critical temperature,

if one may judge from the Brinell hardness values quoted in their paper, and were therefore in the martensitic condition ; they were comparable, in fact, with the samples tempered at 500°C. whose corrosion values are plotted in Fig. 153. On the other hand, the author's samples tempered at 550°C. —see Fig. 153 —had reached this critical tempering range with a consequent decomposition of the martensite to exceedingly fine sorbite. If, as seems probable, the greater susceptibility to attack found at either 550°C. or 593°C. is due to the precipitated carbide being in an excessively fine state of division, it is likely that the maximum effect will be found near 550°C. rather than 600°C.

All the results plotted in Figs. 151 to 154 were obtained on separate pieces, each of which had been tempered uniformly ; the values obtained therefore represent what may be regarded as the intrinsic susceptibility of each state of tempering of a given steel. If, however, all these states occur in the same piece of steel —a condition of affairs which would be produced if a hardened piece were tempered locally at 700°C. or thereabouts —the differences in rates of attack are likely to be still greater, owing to electrochemical effects. There is evidence that this is the case, and actually the unavoidable production of this less resistant band in a hardened article which has been tempered locally is the most noticeable form of its occurrence in practice. The tempering of the whole of an article at 550°/600°C. is undesirable on mechanical grounds and therefore likely to be an infrequent occurrence ; on the other hand, the production of articles which are hard in one part and soft in another is not by any means infrequent. It has given rise, for example, to considerable trouble in the cutlery trade.

The corroded bands on the knives in Fig. 155 may be seen in the very early stages of development on stainless steel knives in many hotels and restaurants. Still more careful observation will reveal the fact that they are not found on knives fitted with ivory or celluloid handles but are almost exclusively confined to those to which metal handles have been brazed. This provides the explanation of their cause. During manufacture, the blade is hardened and tempered and afterwards the handle is fitted. During the brazing operation, the tang and bolster of the knife are heated to some temperature above that at which the steel hardens, with

Plate XXVIII

Fig 155 — Corroded bands on stainless steel knives fitted with brazed on handles (The round dots on B are Brinell impressions)

(To face page 270)

the result that the heat runs down past the bolster into the blade and at some spot, generally within an inch of the bolster, the material reaches a temperature between 500° and 800°C. and hence produces a soft spot. The corroded band is formed close to the junction of this soft band and the hard blade, i.e., the part which was heated to 550°/600°C. The existence of this soft band can often be detected on a still incorroded blade by the greater depth of the fine scratches, developed during use, which cross it.

Fig. 156 represents a series of bars which were tested to prove the truth of this argument. They were air hardened throughout and were then taper heated, the numbered ends of each bar being raised to a temperature of 950°C., the other
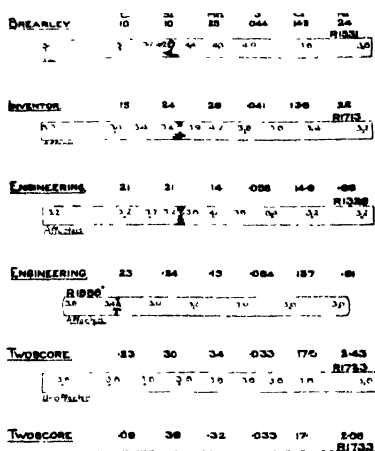
Fig. 156. Effect of local tempering on corrosion of stainless steels. The bars were air hardened throughout and then reheated at the numbered ends to 950° C. (the other ends being kept cool) and again air cooled. They were then polished and immersed in a cold 3½ per cent. solution of sodium chloride for 20 weeks. (N.B.—Sample R.1686 was taper heated to 750°C. only.)

ends being meanwhile kept at atmospheric temperature, and the whole bar then again air cooled. The bars, after being ground and polished, were immersed in a cold 3½ per cent. solution of salt for 20 weeks. A corroded band, the first signs of which were visible in a few hours, was produced on each bar except the two containing 17/18 per cent.

Plate XXX

Fig. 159 — Stainl.... steel plate locally heated with blowpipe and etc
with ferric chloride.   page 273

Fig. 160 — Stainless steel blade with " brazed-on " handle, etched with
ferric chloride, showing soft band.

is often carried out and many hundreds of rams, so treated, have been put into service.   It should be remembered, however, that there is bound to be a band somewhere between the hardest and softest parts where, during tempering, the temperature attained was 550°/600°C., and this band has a lower resistance to corrosion than the material on either side of it.   It may be that the lessened resistance will not cause any trouble, there is in fact ample evidence that in many instances the resistance possessed by this band has been quite sufficient for the particular corrosive conditions encountered ; but if it should happen that corrosion occurred at such a band, Fig. 156 indicates that the remedy is to use a steel of higher chromium content, such as the 17/18 per cent. samples referred to in that diagram.   It should not be inferred that varying heat treatment has absolutely no effect on the corrosion resistance of even such high chromium steels as these, but it is evident from Fig. 156 that whatever difference may exist is not sufficient to cause any attack on the steel even under the very severe conditions referred to in this diagram.

A means of determining the presence and location of such a soft band is obviously of interest, particularly if it may be carried out without seriously damaging the article concerned. Experience indicated that a one per cent. solution of ferric chloride, used as an etching reagent, provided such a means. Fig. 159 represents a piece of stainless steel (containing about 0·3 per cent. carbon and 13 per cent. chromium) which was first hardened throughout, then locally heated by an oxy-acetylene torch, and afterwards polished and etched with the ferric chloride solution.   The parts heated by the torch to a temperature high enough to cause them to harden are only slightly attacked and hence appear light in the photograph ; those not heated above about 500°C. behave in a similar manner but where the temperature attained was just sufficient to soften the previously hardened sheet, the etching action is more rapid, with the result that the surface appears relatively dark.   Notice particularly where the long, heated band has softened the previously heated, shorter bands.

A stainless steel knife blade, fitted with a brazed-on handle, when etched with the ferric chloride solution, gave the result shown in Fig. 160.   The small Brinell impressions visible on the blade reveal the relative softness of the darker band.

One other form of taper heating may be mentioned. In the experiments described in Figs. 156 and 157, the bars contained all gradations in structure produced on the one hand by tempering a fully hardened sample at all temperatures up to the Ac.1 point and also those which occur as the temperature is further raised through the hardening range, until full hardness is attained. The tests on these bars showed the weakest spot to be where tempering commenced. What of the other progressive change through the hardening range? Would any similar band of lower resistance be found if only this range were present in a bar? Fig. 161 shows that if a bar of "cutlery" quality steel be hardened and then tempered throughout at 700°C., or thereabouts, and afterwards one end raised to 950°C. and the whole air cooled, it will show a band of lower resistance at the point at which it commences to harden. In this case, however, the effect is very slow to develop (the corrosion band in Fig. 161 began to be visible after immersion in the salt water for rather more than 2 weeks as against a few hours in the case of the bars in Fig. 156), indicating that the difference in corrosion resistance is very slight. It may be noted that tests on small samples of the same steel as that used for Fig. 161 showed that a Brinell hardness number of 302 (the hardness value at the corroded band) was produced by air cooling from 825°C., a temperature somewhat higher than the Ac.1 point of the material.

The sample used for Fig. 161 represents the structural conditions which would be produced adjacent to a weld in a previously softened sheet of stainless steel. On mechanical grounds, it is of course highly undesirable that a weld should be left in this structural condition : the hardened parts would be brittle, and toughness and ductility should be restored by tempering. Fig. 161 indicates that the tempering operation is desirable also on the grounds of resistance to corrosion.

ANNEALING. It has been shown that the microstructure obtained on annealing the hardenable stainless steels at a temperature above the carbon change point but insufficiently high to dissolve all the carbide, is granular, being very similar to that obtained from the same steel after being hardened and then tempered at 700° to 750°C., except that the carbide granules are fewer in number and larger in size. In this

Plate *XXXI*
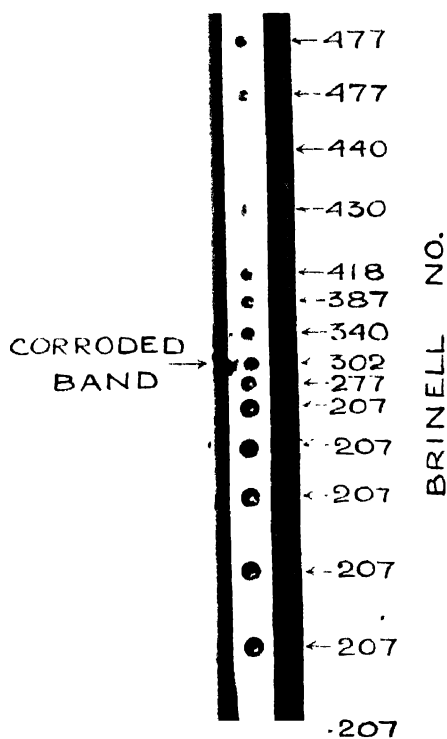
FIG. 161. Taper heated bar of steel containing 0·32 per cent carbon, 12·7 per cent chromium, showing hardness values and corroded band due to 10 weeks' immersion in sea water. The bar was hardened and tempered throughout and the upper end then heated to 950° C, and air cooled

condition, the material is much softer than when hardened and fully tempered and it is somewhat less resistant to corrosion than the latter form.

The non-corrosive properties of material annealed at a sufficiently high temperature to give a pearlitic structure are of comparatively little importance. The mechanical properties associated with such a structure being comparatively poor, it is hardly probable that material would be consciously put into service in such a condition. On general theoretical grounds it would be expected that a given steel would have less resistance to corrosion in such a condition than after any other form of heat treatment, and experiments confirm this.

As illustrating the difference between annealed and hardened and tempered material, the following results of vinegar tests may be of interest. Steels of the following analysis : --

	Carbon %	Chromium %
A	0·31	11·1
B	0·32	12·2
C	0·33	13·3
D	0·31	14·4

were tested, after heat treatment in various ways, with vinegar, in the manner described on page 264. After hardening from 900° to 950°C., all four steels were quite stainless. When fully tempered at 750°C., A stained, B had a very slight stain but was in fact almost stainless, while C and D were quite unstained. After annealing at 900°C., A, B and C were stained by the vinegar while D was practically stainless. Similar results were obtained by annealing at 1,050°C.

The etching effects of picric acid on samples for microscopical examination. which were noted in Chapter II (page 49) have also an interesting bearing on this point. In general, it is found that the ordinary alcoholic solution of this acid which is used for etching carbon steels, has no effect on a 12/14 per cent. chromium stainless steel when this is either hardened or hardened and tempered. The same steel in the annealed condition, however, may as a rule be etched by this solution, though somewhat slowly.

It may be concluded, therefore, that these hardenable stainless steels containing 12/14 per cent. chromium are somewhat less resistant to corrosion when annealed than

when hardened and then tempered in the range 600°/750°C. At the same time, Curve A in Fig. 153 indicates that the differences between these conditions are relatively small and that actually the least resistant form to the attack of salt water is produced by tempering the hardened steel at 550°C.

The effect on corrosion resistance produced by annealing becomes less as the carbon content of the steel is reduced or the chromium content raised. As a result, the corrosion resistance of stainless irons containing more than about 14 per cent. chromium is not noticeably affected by any form of heat treatment; a similar remark applies to the "Twoscore" type of steel (containing 17/20 per cent. chromium and 0·1/0·3 per cent. carbon) as is indicated by curves B and C in Fig. 153.

(B) Austenitic Steels.

When the austenitic chromium-nickel steels were first put on the market in this and other countries, they were hailed as solving many of the problems which the chemical engineer had encountered when using the plain chromium steels and irons. They possessed an adequate resistance to a much wider range of chemicals than did the other class and, moreover, their resistance was held to be less affected by variations in heat treatment or by cold work. In addition, they possessed certain advantages from a constructional point of view; owing to their complete freedom from air hardening effects and their retention of great ductility and toughness when made very coarsely grained, they appeared to be ideal for welding operations, and as a fact welds made in these steels are remarkably tough and ductile. If judged solely on the score of mechanical properties, such welded joints would not require any subsequent heat treatment. As a consequence, many articles and parts of equipment for various chemical purposes were fabricated from these steels by welding and were put into service without further treatment. Again, the belief that variations in heat treatment conditions produced little, if any, effect on the resistance of the steel to corrosive attack led to other parts of fabricated articles, such as screws, bolts and nuts, being manufactured from bars which had been deliberately rolled at temperature between 1,000°C. and 800°C. (or even lower) in order to work

form of the steel; but the differences may not appear to
be very great.   For example, the curves in Fig. 165 refer to
samples so treated after testing in dilute sulphuric and nitric
acids.   These results, however, give no real indication of
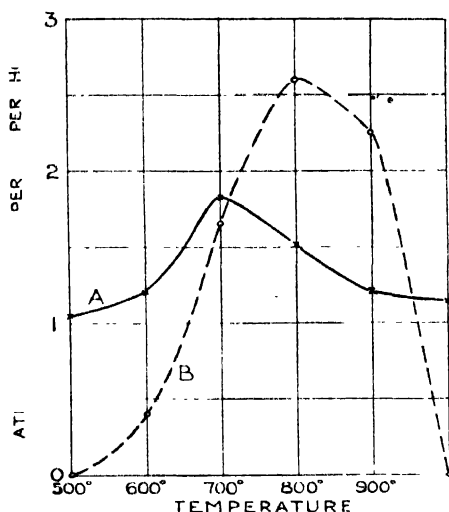
FIG. 165.   Carbon 0·11 per cent.; chromium 14·9 per cent.; nickel
10·9 per cent.   Effect of reheating for 30 minutes to temperatures indicated
on rates of attack of :—
    A.   10 per cent. sulphuric acid at 15° C.
    B.   N/2 nitric acid, boiling.

the damage done to the steel by reheating it in the range of
temperature described.   A better idea will be obtained if
the surfaces of the corroded samples be closely examined ;
that of the fully austenitic sample is quite smooth and firm ;
the reheated samples, on the other hand, will be found to be
rough and possibly loose.   The contrast between the samples
will be increased if they are locally distorted, e.g., by com-
pressing ; the looseness of the reheated samples will be then
much more apparent.   The appearance of the microstructure
in Fig. 166, taken from a section carefully cut through a
corroded surface, shows the reason for this ; the attack on
the sample has proceeded via the grain boundaries to such
an extent that the surface layers have become merely a
collection of loose grains.   The fact that an intergranular
attack can penetrate almost completely through a sheet or
plate without any very noticeable indication of damage being
produced on the metal surface, makes this form of corrosion

Plate XXXIII
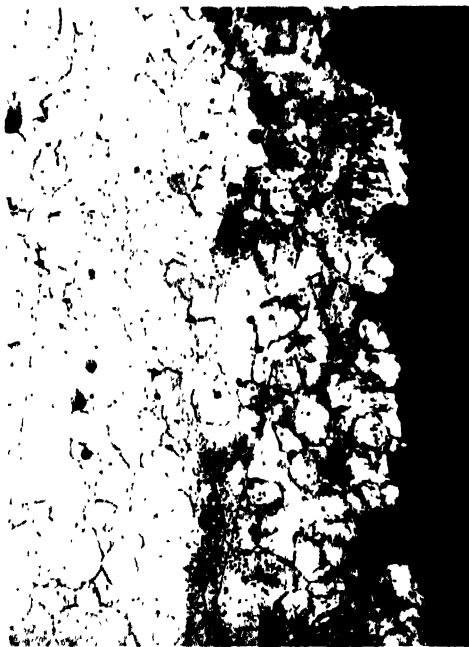
Fig. 166   Austenitic steel containing intergranular carbide films.
Surface of sample after immersion for 4 days in boiling N 2 nitric acid ;   × 100.

Plate XXXIV
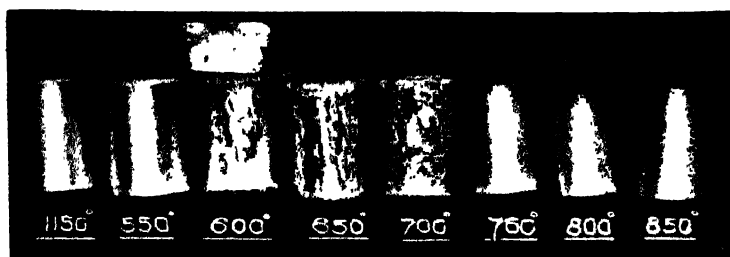
Fig. 167   Series of samples used in testing for intergranular weakness, after bending   The small pieces on the 600 C specimen are corners broken off this sample
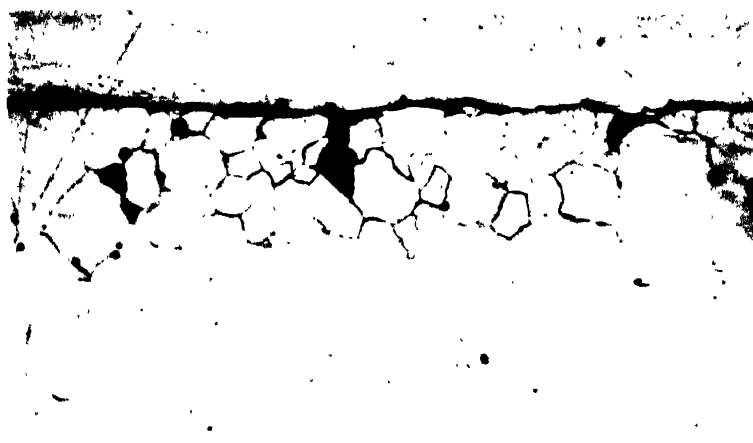
Fig. 168   Corrosion round grain boundaries of 700 C specimen in Fig 167.   × 100

particularly dangerous in chemical equipment. An inter-
granular attack can, of course, be readily shown by bending
a sample thus attacked, but one does not usually treat
parts of equipment in this manner as a periodical inspection
during their life.

It seemed very desirable to have some standardised
means both of determining the susceptibility of various
steels to this type of intergranular breakdown and of judging
the relative effects of various forms of heat treatment in
producing or eliminating it. The following method, worked
out by one of the authors' colleagues, Mr. H. Bull, has proved
very useful in this respect. The steel to be tested is pre-
pared in the form of strip ($1'' \times \frac{1}{8}''$ is a convenient size) and
pieces 3 inches long are heat treated in various ways. They
are then immersed in a 5 per cent. solution of ferric sulphate,
containing also 0·1 per cent. sulphuric acid, in a flask fitted
with a reflux condenser and the solution boiled for 24 hours
or longer. The corroding fluid employed should have
practically no action on the steel in the fully austenitic
condition and only a slow action on the incorrectly treated
form ; if it had a rapid action, the selective intergranular
effect would probably be masked by a general attack. The
solution chosen appears to have the necessary properties.*
At the end of 24 hours or longer, the samples are removed
from the flask, washed and dried and then dropped on to a
hard wooden floor. A good sample rings like a bell, but if
any intergranular attack has taken place, the sample loses
its " ring " ; it sounds, in fact, just like a piece of lead.

Confirmation of the presence or otherwise of intergranular
attack may be obtained either by bending the strips or by
examining microscopically sections cut from them. An
example of the former method is illustrated in Fig. 167 and
shows very plainly the disintegration produced in the speci-
mens reheated to 600°, 650° and 700°C. Fig. 168 indicates
the condition at the surface as seen in a lightly etched cross
section at a magnification of 100 diameters ; as in Fig. 166,
the surface consists merely of a collection of loose grains.

Fig. 167 is important in another respect. It indicates

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* A solution of 111 grams of copper sulphate crystals and 98 grams
concentrated sulphuric acid (S.G., 1·84) in a litre of water also acts in a similar
manner. It has a more drastic action than the ferric sulphate solution. It should
be noted that samples free from carbide films remain quite sound after prolonged
exposure to either of these solutions. They may be attacked to some extent but do
not show any signs of intergranular weakness.

that although precipitation of carbide occurs over a temperature range which extends from 900°C. down to at least 500°C., and possibly lower, the conditions which lead to intergranular attack are produced most easily between 600° and 700°C. Probably at lower temperatures the precipitation of carbide becomes very sluggish while at distinctly higher temperatures than 700°C., the tendency of the carbide to ball up and thus produce a discontinuous chain of particles, instead of a continuous film, at the grain boundary may largely account for the smaller damage produced at these temperatures.

There is also another factor which may exercise a considerable influence on the relative effect of carbide precipitation at 600°/700°C. and at higher temperatures. In the former range, diffusion in the solid steel takes place but slowly ; one may assume, therefore, that the carbide precipitated round the grain boundaries is mainly formed, at least as regards its metallic constituents, from the steel in its immediate vicinity. It is known that this carbide consists largely of chromium carbide—if Kalling's results on chromium steels are assumed to be applicable also to these chromium-nickel steels, the carbide will contain about 65 per cent. chromium—hence its precipitation will lower considerably the chromium content of the metal immediately surrounding the carbide film. Owing to slowness in diffusion, the deficiency in chromium is not made good from areas further away and hence the metal bordering the carbide has its corrosion resistance lowered very markedly. It seems very probable that the lowered resistance of this band, coupled with electrochemical effects due to juxtaposition against a strongly electronegative carbide, accounts for the rapid attack which it suffers when exposed to many corrosive fluids and which is so marked a feature of Fig. 164.*

On the other hand, metallic diffusion occurs much more rapidly at 800° or 900°C. ; hence at these temperatures, the chromium content of the impoverished areas immediately bordering the precipitated carbide particles is rapidly raised by diffusion from surrounding unaffected areas. Although steel treated at these temperatures may have its general resistance to corrosion lowered to some extent by the

* A similar conclusion as regards the effects of reheating to various temperatures has been reached by Bain and Aborn. "The Nature of Nickel-Chromium Stainless Steels." *A.S.S.T.*, Sept., 1930 (preprint).

Plate XXXV
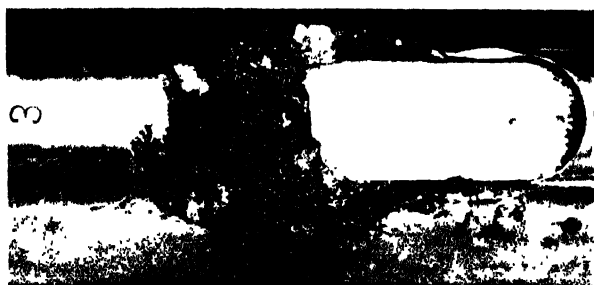
FIG. 169. Intergranular corrosion in pump shaft of wrongly heat-treated austenitic steel (17·7 per cent chromium ; 7·55 per cent nickel) after 2 months' exposure to hot brine.
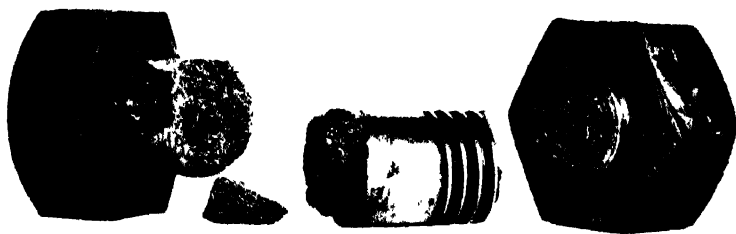
FIG. 170. Intergranular cracks in austenitic steel containing 0·08 per cent carbon.

precipitation of carbide thereby produced, it does not contain local areas whose stability against attack has been greatly reduced.

It has been suggested that intergranular attack is produced by a few corrosive chemicals only ; this is not the author's experience. In one of the first examples of its occurrence in practice, the affected part, a welded vessel, had been exposed to the attack of boiling water containing only traces of sulphuric and nitric acids. Two further instances may be mentioned. Fig. 169 represents the appearance of a pump shaft of steel containing 0·18 per cent. carbon, 17·7 per cent. chromium and 7·55 per cent. nickel after working in warm seawater for three months. Owing to a mistake at the engineering works where this shaft was prepared and used, it had been given the heat treatment operations (air-hardening from 950°C., followed by tempering at 650°C.), suitable for a hardenable steel. The result on the austenitic steel was disastrous ; the separate crystals on the surface could be scraped off with the finger nail and, on attempting to bend the shaft at the corroded part, it broke sharply with a fracture which was very largely intergranular It was obvious that the corrosive effect had penetrated to the centre of the bar.

The bolt in Fig. 170 was of " Anka " steel and, along with a number of others, had been machined from rolled bars which had not been subsequently heat treated. The bars, after rolling, were cooled on the mill floor and it is quite possible that a number of them may have been stacked together in a heap ; their rate of cooling was, at least, sufficiently slow to cause the production of carbide films round the austenite grains. The bolts were used for holding together the sections of an " Anka " tank containing a 5 per cent. solution of nitric acid for pickling purposes (see page 493). Owing to the method of construction of the tank, the bolts were only exposed to the action of such small amounts of the acid as might be splashed on them during the removal of pickled articles from the tank or might leak through the joints of the latter. The tank was also near to another which contained hot, dilute sulphuric acid so that the bolts were probably subjected to fumes and splashes from this acid as well. After two years' service, it was found necessary partially to dismantle the tank in order to remove it to a more

would appear to be to reduce the carbon content of the steel to such a low figure that no precipitation of carbide would occur at any temperature.   It has been stated* that if the steel does not contain more than 0·07 per cent. carbon, no precipitation of carbide occurs on reheating to temperatures below 900°C., e.g., for welding operations, the inference being that this amount of carbon is soluble in the steel at all temperatures.   Apart from the great difficulty, to say the least, of commercially producing material with so low a carbon content, the fact that the bolts illustrated in Fig. 170 contained only 0·08 per cent. carbon suggests that 0·07 per cent. is considerably too high as a limiting value for the carbon content of material not subject to intergranular attack. It is, of course, highly probable that these austenitic chromium nickel steels will retain a small amount of carbon in solution even after reheating to 600°/700°C., the temperature range which appears to produce the intergranular films most readily, but it seems certain that the limiting value is considerably less than 0·07 per cent., probably about 0·03 per cent. is nearer the mark.

More recently Dr. Strauss and his colleagues have published data† indicating that a lower carbon content than 0·07 per cent. is necessary to prevent carbide precipitation. These investigators did not actually use a corrosion test, such as that described on page 279, as a means of determining the effects of composition and heat treatment ; in place of this they measured the potential of the samples, while immersed in normal sulphuric acid in an atmosphere of hydrogen, against an N/10 calomel electrode.   Three steels containing respectively 0·04, 0·06 and 0·12 per cent. carbon (their chromium and nickel contents being 18·0/18·6 and 8·4/9·3 per cent. respectively, were employed and samples of these were heated for ten minutes at 500°, 600°, 700°, 800°, 900° and 1,000°C. and then quenched in water.   All the samples of the two lower carbon steels had the same potential, + 0·84/0·86 volt on the hydrogen scale.   The pieces of the highest carbon steel which had been heated at 500°, 900° and 1,000°C., had a similar value.   On the other hand, the potential of the samples of this steel which had been heated

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* British patent 305,654 (December 24th, 1929). F. Krupp, A.G.

† " Die Carbidausscheidung beim Glühen von nichtrostendem unmagnetischem Chromnickelstahl." B. Strauss, H. Schottky, and J. Hinnüber. *Zeit. f. Anorg. u. Allgem.-Chem.*, Vol. 188 (1930), p. 309.

at 600° and 700°C. dropped to − 0·15 volt, while that treated at 800°C. had been slightly lowered, actually to + 0·3 volt. The experiment was then repeated on a further set of test pieces which had been held at their respective temperatures for 3 hours, instead of 10 minutes. The results obtained from the steels containing 0·04 and 0·12 per cent. carbon were similar to those given by the samples of these steels treated for the shorter period. On the other hand, the steel containing 0·06 per cent. carbon, whose potential had been unaffected by 10 minutes' heating, now showed a decided drop at 600°C., a value of − 0·07 volt being obtained ; the sample treated at 700°C. was practically unaffected (+ 0·32 volt).

Still more recent work by E. C. Bain and R. H. Aborn* shows that the amount of carbon retained in solution in these steels at temperatures below 800°C. is not more than 0·03 per cent.

A second obvious method of attack would be to add to the steel other metals which would either increase the stability of the solution of the carbide in the austenite, and thus prevent, or retard, precipitation in the range 500°/900°C:, or else cause the precipitation of some carbide other than that of chromium and hence eliminate the impoverishment in chromium of the metal immediately surrounding the precipitated carbide. Claims† have been made that the addition of 0·3/1·5 per cent. tungsten to the steel prevents the latter being subject to intergranular attack. Similar claims on behalf of titanium (0·1/2·0 per cent.)‡ and vanadium (0·3/2·0 per cent.)‡ have also been made ; in this case the formation of a carbide other than that of chromium is alleged as the cause of the beneficial action of the added alloys. The minimum amount of titanium or vanadium required in the steel is regulated by its carbon content and is stated to be at least twice as great as the latter. Although the methods claimed in these patents are a step in the right direction, experiment shows quite clearly that the steels containing these added metals are by no means entirely free from this troublesome defect. The precipitation of carbide is retarded, so that a longer exposure in the dangerous temperature range

* *Loc. cit.*

† British patent 316,964 (August 1st, 1929). W. H. Hatfield and H. Green.

‡ British patent, Appl., 22875 (July 25th, 1929). F. Krupp, A.G.

is required in order to produce intergranular weakness, but the samples shown in Fig. 171 indicate that the latter is not eliminated. The six specimens shown in the lower part of the photograph were from a cast containing 0·15 per cent. carbon, 18·1 per cent. chromium, 9·3 per cent. nickel and 0·74 per cent. tungsten and, after having been made completely austenitic, they were reheated to the temperatures indicated for half-an-hour. They were then immersed in a boiling solution of copper sulphate containing some free sulphuric acid* for 3 days. At the end of this period they were tested for soundness by dropping on to a wooden floor, as described earlier ; the samples reheated to 600°, 650° and 700°C. had lost their " ring " and, on being bent, developed the cracks shown in the photograph. As a confirmatory test, further samples were prepared from two other casts, each containing about 1 per cent. tungsten ; these, after being heat treated as described above, were left in the boiling acid copper sulphate solution for 24 hours only. Again, the samples treated at 600°/700°C. developed intergranular cracks, the appearance of the two specimens in the middle of Fig. 171 (one specimen from each cast) being typical of all the pieces heated in this range. Finally, the two samples shown at the top of the photograph represent two different casts containing respectively 0·45 and 0·50 per cent. titanium (their carbon content being 0·14 per cent.). These pieces had been held at 700°C. for half-an-hour and then immersed in the boiling acid copper sulphate liquor for 24 hours. A precisely similar result was obtained from material containing 0·77 per cent. vanadium. Although the titanium steels seem to be considerably better than the tungsten steels, they are not by any means free from attack. In a recent paper, however, Houdremont† claims that steel made in accordance with Messrs. Krupps's second patent was quite free from intergranular attack after being held for 50/100 hours at 600°/700° C. and then immersed for 2,500 hours in the boiling copper sulphate-sulphuric acid reagent.

It may be urged, on the one hand, that half-an-hour is a long time to reheat samples in the dangerous range, because in many fabrication processes the material need only be exposed to this range for a much shorter period than this

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* See footnote on page 279.

† Kruppsche Monatshefte, Nov., 1930.

Plate XXXVI

A   B

600° 650° 700° 800° 900° 1000°
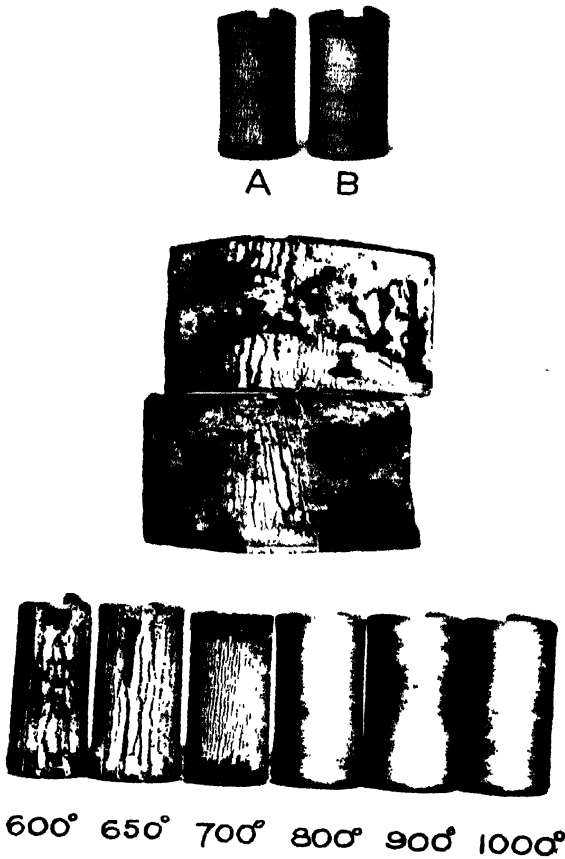
Fig. 171.   Tests for intergranular attack.
Bottom row. Steel containing 0·15 per cent carbon ; 18·1 per cent chromium ;
    9·3 per cent nickel, 0·74 per cent tungsten, reheated for 30 minutes at
    the temperatures indicated
Middle row.   Samples from two further casts containing about 1 per cent.
    tungsten, reheated for 30 minutes at 600 700° C.
Top row.   Samples from two casts containing :
    A   0·14 per cent carbon ; 17·2 per cent chromium ; 10·1 per cent.
    nickel, 0·45 per cent. titanium.
    B   0·15 per cent, carbon ; 17·2 per cent chromium ; 10·1 per cent.
    nickel ; 0·50 per cent. titanium.
    Reheated for 30 minutes at 700 C.
    All the above samples were tested for 24 hours in the boiling copper
sulphate-sulphuric acid solution and then bent.

and, on the other hand, that the acid solution of copper sulphate is an extremely corrosive test reagent which might conceivably produce intergranular breakdown in samples which would remain unaffected in practice under less severely corrosive conditions.   With regard to the time element, it seems very desirable in laboratory tests to adopt, as a measure of safety, a time which is distinctly longer than appears to be necessary for a welding operation.   In many welded vessels, two or more welds meet at one place ; also, welds are not always perfect at the first attempt, occasionally porous areas require filling up.   It must be remembered that the effects of two or more welding operations at the same spot are additive as regards their production of carbide films. There is also a further point ; distortion is not unknown in welded vessels (the high co-efficient of expansion of the steel is largely responsible) necessitating cold work in order to restore the vessel to its desired shape.   Experiment shows that the tendency for intergranular attack to occur is greatly intensified by cold work ; for example, steel which was liable to slight intergranular attack, owing to the presence of a small amount of carbide, would very probably be attacked much more rapidly if it were cold worked.   Pilling,* for example, showed that even a 5 per cent. reduction by cold rolling had a very marked effect in this direction.   From considerations of this nature, it appears to the author that a reasonable test for determining the susceptibility or otherwise of steel to develop intergranular weakness during welding operations consists in reheating it for half an hour to 600°/700° C., after suitable softening, and then immersing in the boiling copper sulphate-sulphuric acid reagent for 72 hours.   As a matter of interest, however further tests were carried out on the tungsten steels by reheating strips ⅛ inch thick in a bath of molten tin ; the latter was brought to the required temperature (650°C. in this case) and the samples then immersed in it for definite times.   This method of treatment was used in order that the periods during which the several samples were exposed at 650°C. might be known with fair accuracy ; the rate of heating in such a bath is extremely rapid, the strips would certainly reach the temperature of the bath in less

* "Some Effects of Nickel Content on Iron-Chromium-Nickel Alloys." N. B. Pilling, A.S.T.M., June, 1930.

than 15 seconds. Samples of ordinary chromium-nickel austenitic steels and of the three steels containing 0·7/1·0 per cent. tungsten referred to on page 286 were immersed for 2, 4, 8 and 16 minutes in the molten tin bath at 650°C. and were subsequently tested in the boiling acid copper sulphate solution for 70 hours. All the samples of the plain chromium-nickel steel broke down under this test. All the samples of the tungsten-bearing steels which had been immersed in the tin bath for 4 minutes or more also broke down. Of the tungsten-bearing samples which had been immersed in the bath for 2 minutes only, one also broke down after 70 hours' boiling, a second was still sound at the end of this period, but developed cracks after being immersed in the boiling copper sulphate solution for a further 13 days, while the third was still sound after this further corrosive treatment.

As regards the severity of the corrosive medium employed, it seems advisable to use as severe a test as possible for short time laboratory tests, because all the evidence at hand suggests that although less severely corrosive conditions, occurring for example in practice, may require a longer time to produce intergranular cracks in carbide-containing material, they will ultimately produce the same result as the more corrosive laboratory test reagents. It is desirable, therefore, to make laboratory tests as severe as possible in the interests of the chemical engineer or other user.

Recent work by N. B. Pilling* indicates that the susceptibility of the chromium-nickel steels to intergranular attack decreases as their nickel content is raised. Pilling's tests referred to material containing 18 per cent. chromium and this was found to be more stable against this type of attack when containing about 15 per cent. nickel than when the content of the latter was only about 8 per cent. It may be noted, however, that the high nickel alloys which gave the best results in his tests also contained 1·2/1·4 per cent. silicon, the possible effects of which Pilling appears to have ignored.

While these pages were in the press, particulars of a further patent, designed to overcome intergranular weakness, have become available. This† calls for the addition of

* *Loc. cit.*

† British patent 348586, May 4th, 1931.   Appl. Nov. 2nd, 1929.   F. Atkinson and T. Hagon.

silicon, the amount specified being 0·5/6·0 per cent., together with certain heat treatment conditions designed to precipitate carbide deliberately in a form, consisting of evenly distributed, rounded particles, which produces no intergranular weakness. Other metals, e.g. copper, molybdenum, tungsten, titanium or vanadium, may be present if desired but are not essential. Tests on steels, produced in accordance with this patent, showed that after being held for an hour at 600°/700°C. or for that matter at any temperature below that necessary for producing a completely austenitic structure, they remained perfectly free from intergranular attack after immersion for ten days in the boiling acid copper sulphate liquor. This is a notable improvement on the results of the tests illustrated in Fig. 171 and it indicates clearly that welded articles of such a steel could be used perfectly satisfactorily without subsequent heat treatment.

It is unfortunate that the early belief in the fool-proof properties of the austenitic chromium-nickel steels, and the simplicity and constancy of their structure, has proved to be untrue ; in some respects, the behaviour of these steels is the reverse of simple. Meanwhile, the wise course is to ensure the absence of intergranular weakness by heat treating as a final process, equipment made from all austenitic steels except those shown, by stringent laboratory tests, to be reasonably free from intergranular weakness. It may be safe to use a welded vessel of, or equipment fabricated by boiler-maker's methods from, such steels, for example, as those illustrated in Fig. 171, without any subsequent heat treatment. Where all the operations, at every stage, are under the observation and control of one who is well-versed in the peculiarities of the material and, in particular, is well aware of the maximum time it may be exposed to 600°/700° C. without deterioration taking place, it is possible that success may be achieved ; but with the evidence of Fig. 171 and of the tests regarding time necessary to produce dangerous intergranular weakness before him, the author, if he were a chemical engineer, would be very chary about using untreated vessels of such steels. For parts of large scale plant, he would certainly take the safe course and insist on a final heat treatment.

(c) Cold Work.

Although cold work is possibly not strictly a condition of heat treatment, it may be convenient to consider here its effects on the corrosion resistance of stainless material. Most metals, when distorted by cold work, have a greater tendency to corrode than they have in the normal condition. Stainless steels are no exception to this ; the ordinary 12/14 per cent. chromium steel, for example, when severely distorted, rusts comparatively readily, thus a coil of severely cold drawn wire of this material will rust into a solid mass if left exposed to the atmosphere for a few months. The comparative resistance of distorted and undistorted material may be shown, for example, by placing half of a broken tensile test piece of similar steel (which had been polished all over before breaking) in a solution of common salt ; corrosion will commence at the distorted end. The effects of cold work in accelerating corrosion are also shown rather strikingly in Fig. 172. The sample represented here, a piece of 12/14 per cent. chromium steel, hardened and tempered, had been cold stamped on one side with the figures 6 and 1. The stamp marks were afterwards just ground out, the surface polished on fine emery paper and the sample placed in five per cent. sulphuric acid for about eight hours. The distorted areas immediately under the original stamp marks had not been completely removed during the subsequent grinding and polishing operations and these were attacked more rapidly than the undistorted metal, with the result shown in the photograph.

Evans[*] considers that the residual stresses left in distorted metal also play an important part in promoting corrosion in that they keep cracking or distending the invisible protective film of oxide which forms on the surface of the steel and hence reduce its power of protecting the steel from attack.

Whether corrosion will or will not take place under stated conditions in a sample which has undergone a small amount of distortion, depends on the composition of the steel and can only be settled by actual experiment, but the lessened resistance is always produced, just as it is by tempering a hardened sample. It is for this reason that a polished surface on stainless steel is more resistant than a roughly

Plate XXXVII

Fig. 172.   Effect of distortion on the rate of attack of dilute sulphuric acid on 12–14 per cent. chromium stainless steel.

Plate XXXVIII

FIG. 173. Rough machined surface, showing cracks perpendicular to path of tool. × 12.
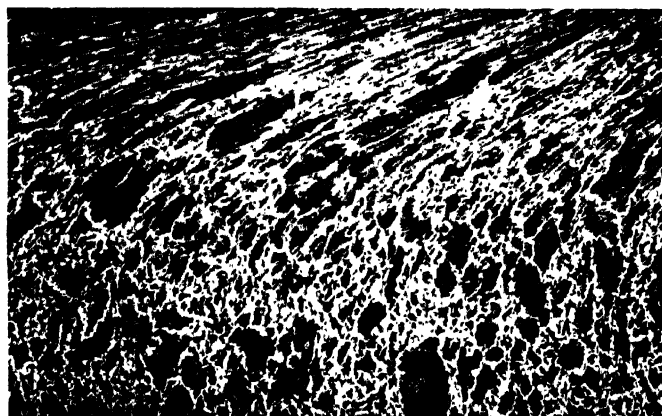
FIG. 174. Cross section through machined surface, showing distorted skin. × 100.

machined surface ; the effect is due, however, not to the presence of polish on the former but to the absence of the distorted skin which is produced by the rough machining. There is also an indirect advantage in a polished surface ; being smooth, it offers less opportunity for the lodgment of dust than a rough surface and, therefore; less chance of local pitting due to galvanic effects which are liable to be produced sometimes by dust.

In order to give some idea of the amount of distortion which may be produced by rough machining, Figs. 173 and 174 are of interest. The former shows the appearance of a planed surface of steel at a magnification of 12 diameters and one can see very distinctly the small cracks, perpendicular to the path of the tool, which are formed as the chips break off. It may be mentioned that the surface shown in Fig. 173 was not by any means very roughly machined, the actual feed of the tool being only $\frac{1}{32}$ inch wide.

The planings or turnings from such a surface are, of course, very badly distorted, but the surface which remains is also distorted and probably cracked for an appreciable thickness, as indicated in Fig. 174, which shows a section perpendicular to a machined surface. It will be seen that the surface is severely distorted in this case for a depth of about a hundredth of an inch. Such an effect is typical of what happens to a varying degree with all rough machining. In order that such a surface as that shown in Fig. 173 could be polished satisfactorily it would have to be finely machined and ground, and both these operations produce surfaces which are very much less distorted than those produced by rough machining.

The effects of cold work in lowering resistance to corrosion are likely to be greater, other conditions being equal, when a sample is deformed locally than if the cold working effects are relatively uniform, as occurs for example in the production of wire or cold rolled strip. The undistorted parts of samples, locally deformed, become electronegative to the d storted areas and hence tend to set up corrosion in the latter, thus increasing their tendency to corrode.

When considering the effects of cold work on the resistance to corrosion of stainless steels as a whole, the influence of composition must be taken into account. It seems obvious that the greater the intrinsic resistance of an alloy to corrosive

attack, the less likelihood is there of it being attacked, under given conditions, after receiving a stated amount of deformation. In the case of the 12/14 per cent. chromium irons and steels, the effects of cold work have always to be kept in mind and manufacturing conditions arranged so as to avoid, as far as possible, leaving the finished article in a severely distorted condition. The more resistant.alloys, e.g., those with higher chromium content or the austenitic alloys of the " Anka-Staybrite-V.2.A." type, may be treated with more
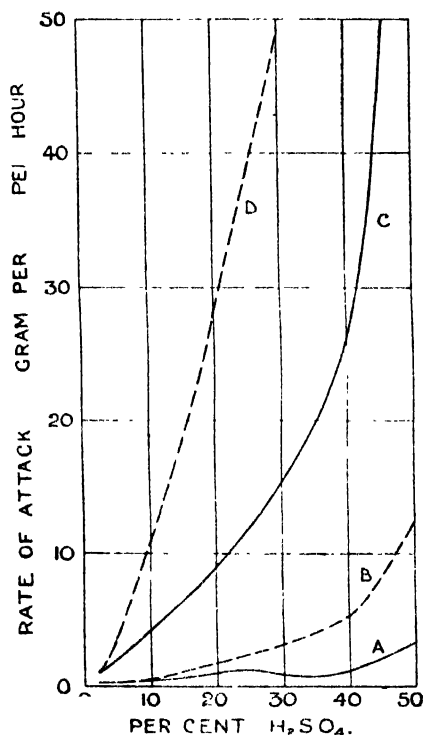
Fig. 175. Effect of cold work on the rate of attack of sulphuric acid on " Anka " steel. The samples used for curves B and D had been previously compressed 20 per cent. of their length.

Curves A and B ... ... Tests at 15° C.
    ,,   C and D ... ... ,,   ,, 40° C.

freedom. For example, the latter type of alloy has been successfully used in the form of wire or cold rolled strip for parts of seaplanes where the severely corrosive attack of sea water is encountered. The fact, however, that the surface stability of even these resistant alloys is lowered by cold

work should be borne in mind, particularly in regard to chemical engineering applications where extremely corrosive conditions may be expected. The data plotted in Fig. 175 refer to the action of sulphuric acid and indicate the lowered resistance produced by compressing samples 20 per cent. of their length. Results of a similar nature are likely to be obtained with other corrosive fluids and other types of corrosion-resistant alloys.

Data indicating the effects of polished and distorted surfaces were obtained by Bannister and Evans* who used a very ingenious method for measuring the potential of metals against a calomel electrode, a dilute solution of potassium chloride being used as electrolyte. They showed that the value obtained for " Staybrite " (18 per cent. chromium, 8 per cent. nickel) varied considerably with the manner in which the surface of the tested sample had been prepared. When the latter was wire brushed, the potential (hydrogen scale) was -0.023 volts ; after carefully polishing with No. 1 French emery paper, a value of $+0.128$ volts was obtained, while a highly polished sample gave the very high value of $+0.510$ volts. These values may be regarded as indicating, in a qualitative fashion, the protective value of the invisible oxide film on the metal surface and hence, while not giving any measure of the velocity of corrosion of the several samples when chemically attacked, may be looked upon as reflecting their " liability to corrosion " when exposed to severely corrosive agencies.

(2) EFFECTS PRODUCED BY VARIATIONS IN COMPOSITION.

Stainless steels are rapidly becoming complex materials containing many different metals, each of which presumably contributes in some way to the special properties possessed by the steels containing them. It cannot be said that it is possible to indicate the quantitative effect of each different metal, contained in a particular steel, on the resistance of the latter to various corrosive agencies—one can only indicate these effects broadly—but it may be useful if a brief summary is given of the tendency which each metal appears to exert on the response of the steel to different forms of corrosive attack. Further details as to the influence of some of the

* " The Passivity of Metals." Part V. *J.C.S.*, June, 1930, p. 1361.

metals will be found in the next chapter, in which the action of specific chemicals is considered.

(a) **Chromium.** From the point of view of resistance to atmospheric attack and to other similar corrosive, agencies,where the main factors are moisture and the oxygen of the air, chromium is undoubtedly the most important constituent of the steel. The higher the chromium content, other things being equal, the greater ·the resistance to corrosion.

Chromium, however, may exist in steel in two forms :--

(a) in solution in the steel ; and

(b) combined with carbon as carbide.

It is only valuable for promoting resistance to corrosion when in solution ; existing as separate particles of carbide, disseminated through the steel, it is so much waste material for this purpose though its presence in this condition may be, and often is, necessary on the ground of desired mechanical properties.

One cannot always, however, determine the composition of a steel solely on corrosion resistance grounds ; very often mechanical properties are of almost equal importance, and these have been shown to be greatly affected by variations in chromium content. Economic considerations also play their part as the cost of the steels, especially if of low carbon content, increases considerably as the amount of chromium they contain is raised. Hence it happens that the selection of the most suitable analysis for specific purposes will often be in the nature of a compromise and that the chromium content securing the best combination of physical and non-corrosive requirements may, and probably will, vary in different cases. This may be illustrated by considering two extreme cases. In the use of stainless steel for cutlery purposes, it is essential that the material shall be capable of hardening to a sufficient extent to function as a useful knife. However resistant to corrosion a knife may be, its use is obviously limited if its cutting powers are no greater than those of a butter knife or a silver fruit knife. It should also possess, when in a suitably hardened condition, sufficient surface stability to resist successfully the attack of such media as it is likely to come in contact with in the course of its every-day use, but, on the other hand, there is no necessity for it to possess such

extreme resistance to corrosion as would be required to withstand such conditions as, for example, the electro-chemical action liable to be set up by contact with copper alloys or graphite while immersed in an electrolyte such as brine. For such cutlery purposes a chromium content of about 12 per cent. gives ample resistance to corrosion and enables the cutler to produce a knife of sufficient hardness to be worthy of the name.

Increasing the chromium to 14 or 15 per cent. undoubtedly gives greater resistance to general corrosion, but to what purpose ? If, as is definitely the case, material with about 12 per cent. has ample resistance for all cutlery requirements, why give it more, especially as by so doing the capacity of the steel for hardening becomes less and, in addition, distinctly higher quenching temperatures, with their attendant difficulties of increased scaling, greater liability of cracking and coarser structure in the hardened knife, are required to produce the maximum hardness the material is capable of giving ?

Actually cutlery, which will have adequate resistance to corrosion to function as truly " stainless " cutlery, can be manufactured from material containing considerably less than 12 per cent. chromium, while, at the same time, the knives made from such material possess a hardness and " springiness " superior to that of knives containing 12 per cent. or so of chromium and practically equal to that which one associates with blades manufactured from first-class shear steel. The author has had a table-knife made from material containing 8·6 per cent. chromium in daily use for the past six years. It has never been repolished and is still in perfect condition, while it possesses a " springiness " which would be a revelation to those accustomed to the very high chromium article. Such lower chromium material probably requires more care on the part of the cutler in producing a stainless knife. Thus, in order that it may be truly stainless, it will need to be hardened from a higher temperature than that required for the steel containing about 12 per cent. of chromium* and it is more likely to suffer through careless grinding. Probably, there-fore, the cutler will prefer to use the higher chromium

* Compare the tests reported on page 264 on a steel of similar chromium, though rather higher carbon, content.

material containing about 12 per cent. or so of that element ; certainly this material is, from his point of view, more " fool-proof " than the other. Such a consideration, both as regards manufacture of the steel and of the knife, may. be the underlying idea in the suggested use of steels containing 14 or 15 per cent. chromium.

At the other extreme, one may consider the case of material to be used for ornamental work or for articles which require no great mechanical strength in the material from which they are made, but which should possess, in as great a degree as possible, resistance to general corrosion. As such articles have frequently to be machined, pressed, or otherwise cold-worked in the course of their manufacture, it is desirable that this exceptionally good resistance to corrosion should be possessed by the material when it is in its softest condition. For such purposes, as high a chromium content as economic conditions will allow is desirable in the material.

Experiment has shown that for many purposes involving resistance to general corrosion or to the attack of foods and condiments, a chromium content of 12/14 per cent. (combined, in the straight chromium steels, with not more than about 0·4 per cent. carbon) is adequate. Material of this type has also the great merit of responding extremely well to heat treatment. Special purposes involving resistance to particularly severe corrosive conditions may, however, call for higher chromium contents than this. Thus a minimum of about 15 per cent. (in actual solution in the steel) seems desirable for adequate resistance to nitric acid while a still higher percentage (17/20) is necessary in hardenable material to secure reasonable immunity from electrochemical effects due to contact with copper alloys while immersed in saline water. A similar content seems desirable when resistance to sea water spray is necessary. Further consideration will be given to all these particular problems in the next chapter, but it may be mentioned that a high nickel content is also helpful in the two last cases, but appears to have no value with nitric acid.

As regards the attack of chemicals, it is not easy to generalise. It has been said that chromium confers resistance to such chemicals as are of an oxidising nature and there is some truth in the remark ; for example, chromium is
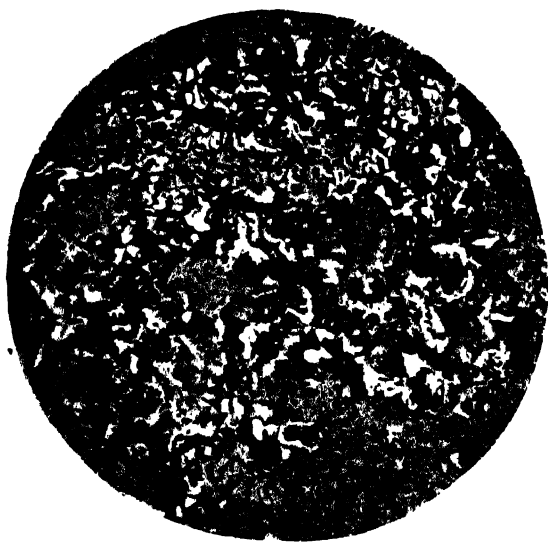
Plate XXXIX

FIG. 176. Corrosion round particles of free carbide in high carbon stainless steel. × 500. · (see page 297).

undoubtedly the main factor in conferring on stainless steels the property of resistance to the attack of nitric acid. On the other hand, acids such as acetic and citric are by no means oxidising acids, but the presence of 12 per cent. or more chromium in steel reduces very considerably the rate at which it is attacked by these acids, although it does not confer complete immunity from their action.

The attack of acids such as sulphuric and hydrochloric, whose action on ordinary steel gives rise to copious evolution of hydrogen, is in general not retarded by chromium; on the contrary, it is often accelerated. The plain chromium steels are generally of no value in connection with such acids.

(b) **Carbon.** On corrosion resistance grounds, carbon is not useful; the less of it there is in the steel, the better. When existing in solution in the latter, it appears to confer no benefit as regards anti-corrosive properties, while if present as separate particles of carbide it is definitely harmful, and for at least two reasons : —

(a) the carbide particles contain about twelve times as much chromium as carbon ; the presence of this chromium in the carbide (where it is of no value from a corrosion resistance point of view) lessens the amount in solution in the steel and hence lowers the latter's intrinsic resistance to corrosion.

(b) the carbide particles are electronegative to the steel and may tend to set up corrosion by electro-chemical action.

The ill effects which free carbide may exert on the corrosion resistance of hardenable steels may be illustrated by noting the behaviour of a 12 per cent chromium steel containing considerably more carbon than usual, e.g., 1 per cent. or thereabouts. Such a steel contains large amounts of free carbide even after quenching from high temperatures and, when tested with vinegar, is likely to stain. Fig. 176 represents part of the attacked surface of a sample containing 11·8 per cent. chromium and 1·0 per cent. carbon ; the sample had been quenched from 1,100°C. and tested with vinegar in the manner described earlier. It will be seen that the dark, deeply corroded areas lie in close proximity to the large particles of free carbide which are visible in the section. A certain amount of carbon is, of course, necessary in hardenable steels to secure desired mechanical

properties.   The latter, however, are also influenced by heat treatment conditions ; hence it should be a rule that as low a carbon content should be selected as will give these desired properties.   For example, assuming 12/14 per cent. chromium steels are in question, a tensile strength of about 40 tons per square inch may be obtained from stainless iron (carbon about 0·1 per cent.) by suitable hardening and tempering, or from steel of about 0·3 per cent. carbon by annealing.   There is no question that from every point of view, the former material is superior to the latter.

In the case of austenitic steels, carbon is generally of no advantage from a mechanical point of view and hence should be as low as possible ; its ill effects when existing as free carbide have already been described.   An exception may be made in the case of those steels which are used for heat resisting purposes and which are required to possess considerable strength as well as resistance to oxidation at high temperatures ; a moderate amount of carbon seems beneficial for the former property.

(c) **Nickel.**   The resistance of mild steel to atmospheric attack is increased considerably by the addition of a large amount of nickel, e.g. 25 per cent. or more ; such high nickel steels had at one time a considerable vogue as corrosion resisting metals although they are not by any means entirely non-corrosive, as anyone may see who immerses a bar of such material in salt water for a few hours. Actually they are inferior in this respect to the ordinary 12 per cent. chromium stainless steel.

The small amounts of nickel—up to 2 or 3 per cent.— found in the ordinary hardenable stainless steels and irons or in the special " Twoscore " steels have no appreciable influence on the resistance of these steels to corrosion.   This may be observed in some comparative tests made on two steels containing :—

	A		B
Carbon ...	0·39 %	...	0·39 %
Silicon ...	0·08 %	...	0·12 %
Manganese	0·10 %	...	0·32 %
Chromium ...	10·0 %	...	10·5 %
Nickel ...	0·42 %	...	2·2 %

The chromium content of the two samples is lower than usual in stainless steels, but this is an advantage rather than

otherwise as it will tend to emphasise any influence that the nickel may have. .

Polished samples of these two steels, both in the hardened condition and also after hardening and fully tempering were exposed to the action of water for four months and in both cases the steels behaved in a precisely similar manner. There was slight local attack on all samples at the point of support, the amount of attack being greater in the tempered specimens than in those which were hard, but no difference was observable between the two steels. Apart from this local attack, the samples retained their initial polish during the test.

The high nickel steel was somewhat more resistant to vinegar than the other, but the difference was very slight.

Samples of both steels, after hardening and tempering, were exposed to the attack of various acids with the results given in Table LXVI, the losses in weight being expressed in grams per square metre of surface per hour* : —

TABLE LXVI.

Effect of 2·24 per cent. Nickel on the Acid Resistance of 10 per cent. Chromium Steel.

Acid.	Strength	Duration of attack.	Rate of attack: grs. per sq. m. per hour.	
			Steel A. 0·42% Nickel.	Steel B. 2·24% Nickel.
Sulphuric ...	5%	6 hours	12·6	11·9
Hydrochloric .	Normal	,,	3·9	9·4
Nitric	,,	,,	93·4	86·6
Acetic	5%	5 days	0·51	0·42
Citric	6%	24 hours	0·35	0·25

The results indicate that the presence of about 2 per cent. nickel has possibly a slight beneficial influence on the resistance of the steel to vinegar and to some acids, but produces no noticeable effect on the resistance of the steel to general corrosion. It is evident that, as a general rule, the effect of such an amount of nickel on corrosion may be ignored and its presence adjusted, if necessary, to suit physical requirements.

* See page 315 for the significance of this method of recording losses in weight.

The much greater amount of nickel present in austenitic steels, however, exercises a very distinct influence on the resistance of the latter to corrosion, and particularly to the attack of chemicals of various kinds. In this respect, nickel differs considerably from chromium in the virtues it confers on the steel to which it is added. Addition of chromium, as has been shown, brings resistance to nitric acid but serves no useful purpose in connection with sulphuric and hydrochloric acids. Nickel, as is evident from Table LXVII, giving results obtained by Dr. Hatfield,* is of no value where nitric acid is concerned but makes the steel to which it is added much less soluble in hydrochloric and sulphuric acids, particularly the latter.

TABLE LXVII.

Effect of Nickel on the Solubility of Steel in Acids.

			Losses in weight in grams.		
Carbon %	Nickel %	Chromium %	Hydrochloric Acid. (conc.)	Nitric Acid. (Sp. Gr. 1·20)	Sulphuric Acid. 10%
0·39	0·41	nil	0·1812	0·5858	0·1032
0·26	4·82	,,	0·1142	0·7398	0·0221
0·16	6·05	,,	0·0872	0·4475	0·0072
0·31	9·02	,,	0·1593	0·6494	0·0102
0·23	12·33	,,	0·1939	0·7123	0·0074
0·32	14·90	,,	0·0816	0·7026	0·0028
0·26	20·08	,,	0·0838	0·6887	0·0010
0·31	24·21	,,	0·0568	0·7532	0·0008
0·18	26·1	,,	0·0678	0·5914	0·0006
0·18	29·3	,,	0·0290	0·7745	0·0005
0·23	36·5	,,	0·0237	0·5730	0·0003
0·29	44·75	,,	0·0329	0·5684	0·0004

Results obtained by Guertler and Ackermann† in an extended series of tests on iron-chromium-nickel alloys showed that the rate of solution of such alloys in nitric acid was almost entirely a function of their chromium content ; when this was constant, addition of nickel conferred no increased resistance to this acid. The same conclusion was

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* *J.I.S.I.*, 1923, II, p. 103.

† *Zeitschrift für Metallkunde*, August, 1928, p. 269.

also reached by Pilling and Ackermann* as a result of tests on a very comprehensive series of alloys. On the other hand, the rates of attack of cold dilute hydrochloric and sulphuric acids on chromium steels were shown, particularly by the latter investigators, to be reduced considerably by the addition of up to about 12/15 per cent. nickel. Addition of still more nickel, even to the point of replacing the iron entirely by this metal, did not effect any further appreciable improvement in the resistance of the alloys to these acids ; although it undoubtedly has a marked effect in this direction when the acids are hot (see page 358). Pilling and Ackermann also found that the high nickel content of the austenitic steels was valuable in reducing the rate of attack of acetic, citric, lactic, formic, phosphoric and tartaric acids but appeared to have little effect on that of oxalic acid.†

The greater resistance of the austenitic steels, such as " Anka," " Staybrite " and " V.2.A.," to sulphuric acid, as compared with steels of similar chromium content but free or practically so from nickel is probably the reason why the former are affected less by industrial atmospheres than the latter. Such atmospheres invariably contain small but distinct amounts of sulphuric acid and are therefore likely to produce a greater amount of pitting in the nickel-free steels.

(D) **Silicon.** The presence of about one per cent. silicon appears to have little effect on the resistance of 12/14 per cent. chromium steel to ordinary corrosion. For example, comparative tests were made on two steels having the following analysis :—

	A		B
Carbon ...	0·39 %	...	0·38 %
Silicon ...	0·11 %	...	1·26 %
Manganese	0·22 %	...	0·28 %
Chromium ...	13·6 %	...	13·8 %
Nickel ...	0·64 %		

After being oil quenched from 900°C., sample A was hard (Brinell hardness number 495) and stainless to the vinegar test ; sample B, after the same treatment was much

* * " Resistance of Iron-Nickel-Chromium Alloys to Corrosion by Acids." *Amer. Inst. Min. & Met. Eng.*, February, 1929. Tech. Pub. No. 174.

† See however the data on page 386 re this acid.

less hard (Brinell hardness number 286) and it stained slightly with vinegar. Raising the quenching temperature to 950°C. increased the Brinell hardness number of sample *A* to 555 and of *B* to 480 ; in this condition both were un-attacked by vinegar. After hardening and tempering, both were stained slightly, *B* less so than *A* ; similar results were obtained after annealing. Samples of the steels were hardened and then tempered at 700°C. and in this condition were immersed in tap water for 8 months ; they were then both perfectly free from any sign of corrosion. Further samples of both steels which had been annealed at 900°C. were also quite unattacked after a similar exposure.

The results suggest that silicon, to the extent of one per cent. or so, has little influence on resistance to corrosion. A similar opinion was given as a result of tests carried out at Woolwich Arsenal* on steels containing high (about 1·4 per cent.) and low percentages of silicon and with carbon up to 0·43 per cent. As a result of these tests, it was stated : " The anti-corrosive influence of silicon was difficult to estimate in the case of steels containing more than 12·5 per

TABLE LXVIII.

Effect of Silicon on the Acid Resistance of 13 per cent. Chromium Steel.

	Carbon %	Silicon %	Chromium %
Steel *A* ...	0·39	0·11	13·6
Steel *B* ...	0·38	1·26	13·8

Acid.		Strength	Loss : grs. per sq. m. per hour.	
			Steel *A*.	Steel *B*
Hydrochloric ...		10%	2·5	2·65
Nitric		Normal	5·6	·2·4
Sulphuric ...		5%	7·1	2·8
,, ...		35%	112	30·8
,, ...		50%	6·0	8·7
Acetic		5%	0·61	0·63
Citric		6%	1·1	0·5
Oxalic		Normal	0·3	0·3

* " Metallurgical Data on Stainless Steels." H. H. Abram. *Chem. & Met. Eng.*, Vol. XXX (1924), p. 430.

cent. of chromium. In certain acid etching reagents, for example, high silicon steels were undoubtedly the more resistant to attack, but in the weather and sea water trials their superiority over low silicon varieties was not evident and, in fact, appeared to exist only in the tempered specimens of the higher carbon varieties."

As regards the attack of acids, silicon appears to have some beneficial effects ; thus the results in Table LXVIII were obtained on hardened and tempered samples of the two steels referred to on page 301 and the results indicate that the presence of about one per cent. silicon reduces the rate of attack of some, but not all, acids on the steel.

Although silicon appears from these results to be beneficial as regards dilute nitric acid, it is detrimental where hot

TABLE LXIXA.

Effect of Silicon on the Resistance of Chromium Steels to Nitric Acid.

Steel.	A.	B.	C.	D.
Carbon %	0·18	0·15	0·09	0·22
Silicon %	0·15	3·5	0·30	3·3
%	8·8	8·7	14·0	14·9

Strength of Acid.	Temp.	Loss · grs. per sq. m. per hour.			
		A.	B.	C.	D.
Decinormal ...	18°C.	11·4	6·54	0·26	nil
	Boiling	669	569	11·3	5·3
Normal ...	18°C.	26	4·5	nil	nil
	85°C.	31·2	11·8	nil	nil
·	Boiling	263	35·5	nil	nil
S.G. 1·2 ...	18°C.	0·03	0·18	nil	nil
	85°C.	1·23	2·28	0·10	0·26
	Boiling	27·9	29·3	1·01	2·53
S.G. 1·42 ...	18°C.	0·035	0·07	nil	nil
	45°C.	0·51	1·18	0·18	0·25
	Boiling	136	84	4·85	8·15

TABLE LXIXʙ.

Effect of Silicon on the Resistance of Stainless Iron to Boiling Nitric Acid.

		Carbon %	Silicon %	Chromium %
Iron *A*	...	0·08	0·24	15·4
Iron *B*	...	0·10	1·10	15·5

Strength of Acid.				Loss : grs. per sq in. per hour.	
				A.	*B.*
N/10	...	...	..	0·33	nil
N/5	...	...	...	0·46	nil
N/2	...	...	...	0·29	nil
N	...	...	...	0·44	nil
2N.	...	...	...	0·44	nil
5N.	...	...	...	0·60	0·44
S.G. 1·42	...	...	...	1·71	10·3

concentrated solutions of this acid are concerned, as will be evident from the figures given in Tables LXIXᴀ and LXIXʙ. In connection with this, it is of interest to note that Evans[*] pointed out that the addition of about 3·5 per cent. silicon to iron caused the latter to lose its passivity in concentrated nitric acid, a sample of such high silicon material being completely dissolved by acid of specific gravity 1·42 under conditions which produced a quiescent state in pure iron.[†]

Benefits following the use of silicon in corrosion resisting steels have been claimed in a number of patents, among the earliest of which are those obtained by Armstrong and by C. M. Johnson. The Armstrong patents,[‡] which are held by the Ludlum Steel Co., relate mainly to iron-chromium-silicon alloys and the field of composition specified is wide, though it was restricted considerably by court decision as a result of litigation, in the United States of America, with the holders of the Brearley and Haynes patents. The Johnson

[*] *J.C.S.*, May, 1927, p. 1038.

[†] Silicon, up to at least two or three per cent., appears to have no similar adverse effect on the austenitic chromium-nickel steels ; see Table LXXX, page 351.

[‡] U.S. patents : 1,322,511 (Nov. 25th, 1919) ; 1,456,088 (May 22nd, 1923) ; 1,513,793 (Nov. 4th, 1924) ; 1,533,782 (April 14th, 1925) ; 1,555,395 (Sept. 29th, 1925) ; 1,683 ₁₁ ; Oct. 2nd, 1928).

patents* are held by the Crucible Steel Co. of America and they cover a group of iron-chromium-nickel-silicon alloys which are made by this company under the name " Rezistal." A detailed description of the properties of some of these steels has been given by Johnson.†

The chief value of silicon appears to be in materials intended for resisting oxidation at high temperatures. Even when present to the extent of only one per cent., it raises very considerably the temperature at which stainless steels begin to scale freely ; further reference to this will be made later.

(e) **Manganese.** It has been asserted on several occasions that the presence of manganese is detrimental to the corrosion resistance of stainless steel, and allusion made to results obtained by Rohn‡ as supporting this belief. Rohn actually carried out tests on two alloys, containing 25 per cent. chromium, to one of which 1 per cent. manganese had been added. Tests in 10 per cent. nitric acid, both hot and cold showed that both steels were equally immune from attack. In the case of acetic and phosphoric acids, the results on the two steels were of the same order of magnitude and very probably such differences as were noted were within the limits of experimental error. Only in the case of hydrochloric and sulphuric acids—two acids against which 25 per cent. chromium steel possesses no useful degree of resistance— was the manganese found to increase to any notable extent the rate of attack. It may be suggested, therefore, that statements such as "an addition of 1 per cent. manganese more than counterbalances the resistance obtained by a 9 per cent. increase in chromium content " and alleged to be based on these figures,§ are much exaggerated and quite misleading.

Although it is doubtful whether the addition of manganese has any beneficial effect on the corrosion resistance of either chromium or chromium-nickel steels, its presence in amounts up to one per cent. or so, seems to be advantageous, in some cases at least, from the point of view of forging characteristics. It is a pity, therefore, that its use for this purpose should be deprecated or even prohibited on account

* U.S. patents : 1,420,707 (June 27th, 1292) ; 1,420,708 (June 27th, 1922) ; 1,617,334 (Feb. 15th, 1927).

† *Trans. A.S.S.T.*, July, 1921, p. 554.

‡ *Zeit. für. Metallk.*, Dec., 1926, p. 387.

§ *Chem. and Met. Eng.*, July, 1927, p. 417.

of the effects of exaggerated statements, such as that quoted above, which appear to have little or no foundation in fact.

(f) **Copper**   This metal is not commonly added to the straight chromium steels ; claims have been made however, notably by Saklatwalla,* that the addition of about 0·5 to 1·5 per cent. copper to such steels very considerably improves their resistance to acids, notably sulphuric and hydrochloric. In experiments carried out to investigate these claims, samples of steels containing :—

		A		*B*
Carbon	...	0·16 %	...	0·22 %
Silicon	...	0·28 %	...	0·28 %
Manganese		0·17 %	...	0·17 %
Chromium	...	12·1 %	...	12·1 %
Nickel	...	0·44 %	...	0·47 %
Copper	...	0·08 %	...	1·20 %

were hardened from 950°C. and tempered at 700°C. and were then exposed to the action of various acids for suitable periods and their losses in weight determined.   The results obtained are given in Table LXX ; the losses, as before, being expressed in grammes per square metre of surface per hour :—

TABLE LXX.

Effect of Copper on the Acid Resistance of Stainless Steel.

Acid.	Strength.	Duration of attack.	Loss : grs. per sq. m. per hour.	
			Steel *A*. 0·08% Copper.	Steel *B*. 1·2% Copper.
Sulphuric ...	5%	7 hours	22·1	10·5
,, ...	35%	6 ,,	265·0	45·0
,, ...	50%	6 ,,	8·8	6·4
Hydrochloric ...	Normal	7 ,,	5·8	1·8
Nitric ...	Normal	6 ,,	7·1	7·6
Acetic ...	5%	24 ,,	0·32	0·16

It will be seen that the copper has a noticeable effect with all the acids used except nitric.   However, although the addition of copper reduces the rate of attack with most of the acids, the copper-chromium steel can hardly be described as an " acid resisting " material.

* " Ferrous Alloys Resistant to Corrosion." *Iron Age*, April 24th, 1924.

More recently copper has been added to the austenitic nickel chromium alloys,* where its presence appears to confer certain advantages, as regards resistance to the attack of some chemicals, e.g., hydrochloric and sulphuric acids and ammonium chloride ; see Chapter VI.

(g) **Molybdenum.** The resistance of chromium-molybdenum alloys to chemical attack, more particularly of acids, was noted by Borchers and Monnartz some years ago. In 1910, they took out a German patent (No. 246,035) in respect of alloys containing 10/60 per cent. chromium, together with 2/5 per cent. molybdenum, claiming for such alloys high resistance to chemical action and also mechanical workability. They also claimed that the molybdenum could be partly replaced by vanadium or titanium.

The addition of about 2 per cent. molybdenum to a 12 per cent. chromium steel retards considerably the rate at which the latter is attacked by many inorganic and organic acids. As an indication of this, the results in Table LXXI may be noted. The tests were carried out at atmospheric temperature

TABLE LXXI.

Effect of Molybdenum on the Acid Resistance of Stainless Steel.

		Carbon %	Chromium %	Molybdenum%
Steel *A*	...	0·32	12·2	nil
Steel *B*	...	0·23	11·6	2·3

			Loss : grs. per sq. m. per hour.	
Acid.	Strength.	Duration of attack.	*A.*	*B.*
Nitric	Normal	6 hours	17·6	6·7
Hydrochloric ...	10%	24 ,,	21·5	2·0
Sulphuric ...	5%	24 ,,	40·9	13·7
,, ...	35%	6 ,,	205	17·2
Acetic	5%	8 days	0·79	0·045
,, ...	33%	10 ,,	0·98	0·089
Citric	6%	7 ,,	2·4	0·08
Tartaric ...	25%	13 ,,	0·43	0·22

* British patents : 201,914 (July 31st, 1923); 267,024 (Sept. 28th, 1926).

and both the steels were in the hardened and tempered condition.

Molybdenum has a similar effect on the austenitic chromium-nickel steels. For example, when added to the extent of 3 or 4 per cent. to steels of the " V.2.A." class, it produces an alloy very resistant to dilute sulphuric acid, even when the latter is hot. Occasions when such dilute acid solutions are used are frequent in the manufacture and use of dyes ; these solutions are extremely corrosive and the commercial application of certain processes involving their use has been made possible by employing equipment fabricated from these alloys.

The chromium-nickel-molybdenum steels are also especially suited for processes in which contact with sulphur dioxide and sulphites at high temperatures and pressures is involved, this particular purpose being specifically claimed in the original patent* covering their manufacture and use. They also possess a greater degree of resistance to certain organic acids, notably boiling acetic acid, than do the parent chromium-nickel steels. Further details regarding this will be given in the next chapter.

(h) **Tungsten.** Like molybdenum, tungsten increases the acid resistance of chromium and chromium-nickel steels, but to a relatively small extent. The use of this metal (together with others) as an addition to such steels forms the subject of a series of patents, obtained by Sir R. A. Hadfield,† in which it is claimed that the resulting alloys resist corrosion by chemical attack at ordinary temperatures and oxidation and corrosion by hot vapours and gases and also possess great strength at high temperatures.

As regards its influence on the rate of attack of acids on 12 per cent. chromium steel, the results in Table LXXII indicate, by comparison with those in Table LXXI, that tungsten is less effective in this respect than molybdenum.

The Hadfield patents referred to above claim the addition of tungsten for its general effect of improving the corrosion resistance of the chromium and chromium-nickel steels to which it is added ; the more specific effect of preventing

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* British patent 201,915 (July 31st, 1923). F. Krupp, A.G.

† British patents : 220,006 (Feb. 9th, 1923) ; 232,656 (Dec. 27th, 1923) ; 313,471 (June 10th, 1929).

TABLE LXXII.

Effect of Tungsten on the Acid Resistance of Stainless Steel.

		Carbon %	Chromium %	Tungsten %
Steel *A*	...	0·82	12·2	nil
Steel *B*	...	0·82	11·6	1·40

			Loss : grs. per sq. m. per hour.	
Acid.	Strength.	Duration of attack.	*A*.	*B*.
Nitric	Normal	6 hours	17·6	25·1
Hydrochloric ...	10%	24 ,,	21·5	5·5
,, ...	50%	24 ,,	69·8	12·8
Sulphuric ...	5%	24 ,,	40·9	25·7
,, ...	35%	6 ,,	205	101
Acetic	5%	8 days	0·79	0·17
,, ...	33%	10 ,,	0·93	0·17
Citric	6%	7 ,,	2·4	0·25
Tartaric ...	25%	13 ,,	0·43	0·48

intergranular breakdown, as was described on pp. 285 *et seq.*, is the subject of a more recent and quite different patent.

The use of tungsten in heat resisting steels—its beneficial effects in this respect are mentioned in the Hadfield patents—will be described in a later chapter.

(i) **Scale.** Although scale is not strictly a variable in composition, it may not be out of place to consider its effects here. Stainless steels, after reheating to high temperatures, whether followed or not by rolling or forging, are coated with a scale consisting of the oxides of iron, chromium and other metals which may be present. This scale is electronegative to the metal and, if it is not removed, will cause local corrosion of the steel in its neighbourhood. It must therefore be removed either by suitable machining or by pickling. Sand blasting does not appear to be so effective; although the greater part of the scale is removed by this treatment, producing a very pleasing surface, small particles of it are liable to be hammered into the surface of the steel by the sand and thus remain to act as potential centres of corrosion.

Sand blasted material may also rust badly from another cause. The sand grains appear to pick up particles of metal

ŏr oxide from the surfaces they abrade and then to deposit some of these particles on subsequently treated surfaces. If the stainless steel be sand blasted by sand which has previously been used on ordinary steels, the sand particles deposit on the stainless steel some of the material they have previously picked from the other steel. As a result, the sand blasted stainless steel surface will very quickly rust superficially if exposed, e.g., to the atmosphere. The trouble may be avoided however, if the sand blasted surface be pickled in 5 per cent. nitric acid ; the latter removes the deposited material but has little or no action on the steel itself.

It is obvious that the finished surfaces of stainless material should be free from roaks, pits or cracks, or even stamp-marks formed by pressing a lettering die into the surface of the hot steel, because such marks or defects will contain scale. Scale occurring in stamp-marks may generally be removed by careful pickling ; it is preferable, however, to etch* identification marks on finished surfaces rather than to stamp them.

It is also evident that no amount of pickling or machining will remove particles of scale present in wild or unsound steel, as fresh particles are exposed with each new surface. It follows, therefore, that articles made from stainless steel which contains much slag or which was unsound in the ingot will never be so satisfactory as those manufactured from properly made steel of similar analysis ; for example, knives made from such unsound steel develop in use a mottled appearance due to the production of minute pits at points where slag or oxide particles are exposed on the polished surface.

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* A suitable reagent for etching stainless steel consists of :

Ferric Chloride ...	...	...	50 grams.
Hydrochloric Acid (conc.)		...	90 ,,
Nitric Acid (conc.)	...	...	3 ,,

THE RESISTANCE OF STAINLESS STEEL TO VARIOUS TYPES OF CORRODING MEDIA

THE RESISTANCE OF STAINLESS STEELS TO VARIOUS TYPES OF CORRODING MEDIA

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When an attempt is made to determine the resistance of some particular metal to the action of different chemicals and then to assess the value of that metal to the chemical industry, three major difficulties at once present themselves. In the first place, how are the laboratory tests to be carried out ; secondly, how are the results of these tests to be recorded so that those who study the records may obtain a true idea of the behaviour of the metal with different chemicals ; and thirdly, how may the results so obtained be applied to commercial practice ?

The easiest way of carrying out a laboratory test is to immerse completely a weighed sample of known surface area in a suitable volume of the corroding fluid, leave it there for a sufficiently long period to obtain a weighable loss, and then calculate this loss in weight in terms of unit area and time. The result may or may not give useful information, depending on many circumstances. The actual experiment is affected by such obvious factors as the condition of the surface of the sample, the temperature of the solution, the rate at which the strength of the active corroding agent is depleted owing to the progress of the action, and the effect of the products of the action on its further course.

The effect of surface condition varies among the different types of corrosion resistant steels, but is probably never entirely absent ; in making comparative tests between different alloys, the surfaces of the several samples should always be prepared in a manner which can be duplicated with fair accuracy. Generally speaking, this can be achieved more easily if they are prepared with the finer emery papers used for metallographical purposes (" 0 " and " 00 " Fortin or Hubert papers are suitable), than if they are machined or machine ground. Particular care should be taken to avoid heating the surface of a sample during its final polishing because, if this occurs, the rate of attack (or at least its

initial stages) of many reagents on the sample is likely to be affected. Samples which have been used for one test should not be used for a further test until they have been completely resurfaced. Immersion in many chemicals, which may or may not produce visible effects on the steel, induces passivity in the latter, and this may seriously affect the subsequent action of the same or some other chemical on the metal. Frequently the passivity effects produced after the first application of some corrosive fluid are sufficient to prevent further attack on the sample if it is re-immersed in the same corroding fluid without being resurfaced. This phenomenon has been frequently noted in the practical application of the steels and is often of considerable importance.

As regards variations in temperature, it has been stated that the rate at which many chemical reactions take place is doubled by a rise in temperature of about $10°$ C., e.g., from $20°$ C. to $30°$ C. As rates of corrosion are fundamentally rates at which certain chemical reactions take place, further comment is unnecessary. It may be mentioned, however, that with some chemicals, particularly acids, there seems to be a critical temperature above which the rate of attack increases much faster than at lower temperatures. The actual position of this temperature depends on the type of steel and of chemical under consideration, but in the case of nitric acid of S.G. $1·42$ or thereabouts, it occurs between $80°$ C. and the boiling point of the acid ($120°/125°$ C.).

Troubles due to depletion of reagent and its contamination with the products of the attack are most difficult to avoid in laboratory tests ; they are particularly evident in those with dilute solutions of active corroding agents, solutions which are often of great importance commercially. Their effects are of course minimised by using an ample bulk of solution and renewing it at frequent intervals, and by stirring the solution or moving the sample continuously by some form · of mechanism, while it is immersed in the reagent. The latter method requires an elaborate " set-up " when a large number of samples are to be tested but probably lends itself more easily to duplication of conditions than when the stirring of solutions is attempted. A convenient arrangement has been described by Frazer, Ackermann and Sands.*

* " Controllable Variables in the Quantitative Study of the Submerged Corrosion of Metals." *Jnl. Ind. & Eng. Chem.*, Vol. XIX (1927), p. 332.

The recording of results presents considerable difficulty. Broadly speaking, attack on a metal may occur in three ways:—

1. An even attack, leading to the removal from the surface of the sample of a layer sensibly uniform in thickness.

2. An intergranular attack, which in its worst form may convert a solid sample into a mass of loose crystals.

3. Local attacks, producing pits.

In the third case, loss of weight figures are only of value in helping the experimenter to arrive at some estimate as to the depth and extent of the pitting produced under the actual conditions of an experiment. It is obvious that a few deep pits in one sample might produce a smaller loss in weight than a much larger number of very shallow pits ; but the former is generally by far the more serious form of attack. Loss of weight figures are of still less value in the second case, as they give no indication as to the depth to which disintegration has proceeded. This form of attack, however, appears to be confined to austenitic steels which, owing to faulty heat treatment, contain a network of carbide round the austenite grains. It is not produced in these steels when they have been correctly treated nor has it been noted in other types of steels.

Only in the first case do the loss of weight figures provide data which are useful as a measure of the relative value of different specimens under similar test conditions. A convenient method of recording results is in the form of grams per square metre of surface per hour. Expressed in this form, they suggest that the rate of attack remains constant both over the whole surface of the sample and during the whole time it is exposed to the corroding fluid and the idea may be carried further by calculating, from the known density of the metal, the thickness of the presumed uniform layer which would be removed in the course of some specified time—e.g., a month or a year. Most corrosion-resisting steels have densities between 7·75 and 7·95 ; if a mean value of 7·85 be assumed, the thickness of this calculated layer removed in the

course of twelve months by different rates of attack is as follows :—

Rate of attack; Grs. per sq. m. per hour.	Layer removed in 12 months.	
	mm.	ins.
0·1	0·11	0·004
1·0	1·1	0·04
10·0	11·0	0·4

It should be clearly understood, of course, that these equivalent layer thicknesses are only theoretical values— their calculation postulates absolute evenness of attack—but they are useful as providing an easily visualised measure by means of which the effect of different rates of attack may be appreciated. They also suggest that a rate of attack of not more than 0·1 gram per square metre per hour is so slow as to justify the metal possessing it being regarded for practical purposes as " completely resistant " ; while if the rate does not exceed ten times this value (i.e. 1·0 gram per square metre per hour) the metal is likely to serve many useful purposes in chemical engineering. On the other hand, if the rate of attack exceeds 10·0 grams per square metre per hour, the metal may be classed as non-resistant.

It should also be noted that when the rates of attack of different metals are being compared under some given corrosive conditions, it is important that the samples used should have approximately the same size and shape. Also, in worked products, the samples should be oriented in the same manner with regard to the main direction of extension of the metal during working. Most worked metals have a more or less distinct fibrous or plate-like structure and the rates of attack on surfaces parallel and perpendicular to this structure are not always the same.

Further difficulties arise when attempts are made to apply the results of laboratory tests on metals in estimating the probable value of the latter for the construction of plant in connection with the manufacture, storage or use of the particular chemical with which they have been tested. In the first place, it is rare that metal equipment so used is entirely immersed in the corroding fluid ; there is generally a liquid-air interface somewhere and corrosion is apt to be

more severe here than elsewhere, particularly if the position of the interface remains sensibly constant.   True, laboratory tests may be made to test the effect of stationary liquid level by partially immersing the samples under test, but it is not always easy to judge the relative attack on a number of metals so tested.   Secondly, corrosive fluids in practice are rarely stationary in the vessels containing them ; they are generally moving, and frequently rapidly.   As a result the strength of the corroding fluid is not likely to be depleted nor its action retarded or accelerated by reaction products, as so frequently happens in laboratory tests ; in addition, effects due to erosion may probably be encountered.   Again, in practice there is frequently more than one active chemical present ; often there are several, whose relative proportions vary continuously, in addition to others present in small amounts as impurities ; and frequently the rate of attack of a chemical on a given metal is appreciably affected by the presence of even relatively small amounts of other substances.

It is well, therefore, to regard laboratory tests as being designed to sort out the metals likely to be of value for a particular process ; and, wherever possible, to supplement such tests by others under practical conditions. possibly on a small scale, in order to obtain a more valuable discrimination between those metals judged as useful from laboratory tests. Where a suggested plant involves a very large capital expenditure, preliminary trials with a small scale plant are particularly desirable ; the extra insurance against failure thus provided is well worth the capital cost of the experimental plant.   If, however, practical tests are not feasible or are not convenient and some decision has to be made on the results of laboratory experiments, it is well to assume that the rates of attack obtained in these experiments may be considerably exceeded in practice and to allow an ample margin of safety in any estimates as to the probable life of equipment.   It is the practice in at least one large chemical works to assume that rates of attack in practice are likely to reach ten times the values found in laboratory tests.

There is also another factor which enters into such estimates.   Laboratory tests are generally carried out on small samples whose structural condition has been carefully controlled.   The same degree of precision as regards structural characteristics is not always feasible in chemical equipment

and possible local acceleration of attack due to the effects of fabrication processes such as, for example, accidental local distortion, should always be borne in mind.

The data given in the following pages are largely based on experiments, extending over some fifteen years, carried out in the author's laboratory and also upon the results attending the use of the various materials in practice. In addition, the published work of other investigators has been freely quoted. A considerable portion of the author's laboratory work was undertaken to obtain data on specific problems. Owing to this, the experiments with some media have been carried out under conditions which are not strictly parallel with those used with other reagents, the conditions in each case being those best adapted to solve the particular problem in hand. Although this introduces a lack of uniformity of conditions which is perhaps not desirable in a series of scientific investigations, it does not lead to any serious difficulty in the practical application of the several series of results.

The various chemicals, whose effects on different stainless steels are here described, represent only a small fraction of those in which the chemical manufacturer is interested or in connection with which he might find these steels useful for the construction of plant. An attempt to deal with such compounds in any degree of completeness would result in a book of encyclopaedic size. The compounds selected for discussion are, however, among those most commonly handled by the chemical manufacturer and the response of the various kinds of stainless steels to their attack may probably be taken as typical of the service which these steels can render.

Atmospheric Corrosion, The association of the name " stainless steel " with a brightly polished knife blade has been largely responsible for the prevalent idea that articles of stainless steel should always be brightly polished and should always retain this polish indefinitely. Doubtless, it is desirable that many stainless steel articles should possess these attributes ; one may place in this category for example, most household fittings, ornamental or otherwise. There are many other purposes, however, where it is not really necessary that a metal article should be given, or be capable of retaining indefinitely, a polished surface ; the desirable

characteristic of such fittings is that they shall not suffer any marked degree of·corrosion.   This distinction in requisite properties is of considerable importance in regard to the possible effects of atmospheric attack on the various kinds of stainless steels.   As a general rule, polished indoor fittings of any normal stainless steel (containing not less than about 12 per cent. chromium) will retain their lustre indefinitely. Many household fittings consist of castings ; in others sheet, tube and possibly small stampings are used.   As castings are probably more easily prepared in the austenitic chromium-nickel steels than in any other type of stainless steel, and the other forms (tube sheet and stampings), at least as easily, this type of material is generally employed for household purposes ; and experience has shown that bathroom fittings, for example, fabricated of " Anka " or " Staybrite " retain their lustre perfectly.   The stainless irons, however, are quite as useful and these, as well as the austenitic steels, have been widely used for hearth furniture and other decorative fittings with perfect success.

The effects of outdoor exposure depend considerably on location.   In the pure atmosphere of the country, stainless steels will remain unaffected for long periods.   Exposure in some urban districts also produces little effect, even near the coast where the corrosive effects of salt spray are also encountered.   Thus Dr. Newton Friend* reports that a bar of steel containing 13·57 per cent. chromium, after being exposed to the sea air at Plymouth for five years, was still in perfect condition, its original excellent polish being retained.   In large towns, however, and particularly in the neighbourhood of works, corrosive conditions of a much more severe character are frequently encountered.   Generally the atmosphere in such places is dust-laden and also contains small amounts of sulphur dioxide and sulphuric acid. Polished samples exposed for long periods under such conditions become coated with a layer of dust which often adheres very tenaciously to the steel.   When the dust is removed, the surface of the steel underneath may still be unaffected but often is found to be pitted, this being probably caused by the combined action of dust and acid.   The pitting, however, proceeds at a very slow rate and though it

* * " The Deterioration of Structures in Sea-Water."   *Dept. of Sci. & Ind. Res.*, Tenth Report, 1930.

may mar the appearance of a polished surface, the actual amount of metal corroded away is excessively small, even after an exposure of several years. For example, the author has had a number of samples of stainless steels of widely differing compositions hung for 7 or 8 years on a veranda outside his laboratory in the steel works at Atter- cliffe, Sheffield. They are, of course, covered by now with a thick brown coating of ferruginous dust ; on scraping portions of the latter away, the original surface of the steel can still be seen though it is marred in every case as a polished surface by the presence of numerous minute pits. The amount of pitting varies in different steels ; thus other things being equal, it is less the higher the chromium content. It is also less in the austenitic chromium-nickel steels than in the plain chromium steels of like chromium and carbon content, a result which might be expected from the greater resistance of the former steels to sulphurous and sulphuric acids. For the same reason, the presence of metals like molybdenum, copper and tungsten, which also lessen the rate of attack of these acids on either the chromium or chromium-nickel steels is beneficial.

It should be noted that these samples have been exposed under extremely severe conditions. The atmosphere is probably as bad as would be found in any industrial district, while the samples themselves have been exposed continuously and have never been wiped or cleaned during the whole period of their test. It seems doubtful whether any type of corrosion resisting steel commercially available will retain a polished surface absolutely unimpaired by pitting for an indefinite time under such very severe conditions. It is probable, however, that the amount of pitting would be much less if the samples were washed or wiped clean periodically. At the same time, although the pitting produced mars the polished surface, the actual amount of corrosion is exceed- ingly small and it is progressing at so slow a rate that no appreciable change in the appearance of the samples can be noticed over periods of several months. The idea expressed in the last sentence—namely, the possession of an exceed- ingly slow rate of corrosion—brings up again the suggestion mentioned earlier, that there are many metal articles for which the absolute permanence of a polished surface is not really necessary ; what is requisite is that they shall not

corrode rapidly.   This may possibly be well illustrated by referring to the use of these metals for the hinges of doors. An ordinary iron or steel hinge exposed to the atmosphere, rusts fairly rapidly and a typical steel hinge, when hung outside the author's laboratory, had rusted so much in the course of about a couple of months that its two halves could no longer be moved relatively to each other ; in other words, its value as a hinge had completely gone.   A hinge of similar shape, but made of stainless iron, containing some 12 per cent. chromium, was still perfectly satisfactory as a hinge after an exposure of over 5 years.   It was certainly coated with a layer of dust and scraping a little of this away revealed a pitted surface of the steel, but neither the film or the pitting affected the movement of the two parts and, as a hinge, it was then quite as serviceable as on the day it was made.

Evidence of the relative permanence of stainless steel as compared with other steels even in industrial atmospheres, was obtained by Dr. Friend[*] who exposed various steels for 7 years on the roof of the Birmingham Technical

TABLE LXXIII.

Atmospheric Tests on Various Steels at Birmingham (Dr. Newton Friend).

Material.	Loss in Weight (Grams).							
	Roof of Technical College (7 years).				Nechell's Gas Works (6 years).			
	No. of Samples	Max. Loss	Min. Loss	Average	No. of Samples	Max. Loss	Min. Loss	Average
Wrought Iron	12	225·8	177·7	201·2	17	232·2	173·2	207·5
Carbon Steel— 0·05/0·32% Carbon.	9	389·4	176·4	287·3	12	417·2	204·5	332·2
Copper Steel—0·15% ...	1	-- ·	—	183·0	2	210·8	204·8	206·8
Stainless Steels— 11·73/13·4% Chromium.	4	5·3	0·6	2·5	4	6·0	1·0	3·35
Nickel Steels— 2·88/5·8% Nickel.	3	128·5	35·8	73·7	3	146·1	86·3	125·5
Nickel-Chrome Steels— 1·89/3·66% Nickel. 0·66/1·08% Chromium.	4	152·1	23·0	73·1	3	146·3	90·2	115·9

[*] *I. & S. Inst., C.S.M.,* 1929, p. 61.

College and for 6 years on the roof of the laboratory of the Birmingham Gasworks at Nechells. The samples were in the form of bars 2 feet long and 1·1/1·8 inches diameter and their losses in weight at the conclusion of the test are given in Table LXXIII.

Dr. Friend reports that the surfaces of the stainless steel bars were stained but were otherwise in perfect condition.

Tap Water is without action on any normal stainless steel or iron. The author has a number of small samples turned from a bar of "cutlery" quality steel (12 per cent. chromium ; 0·3/0·35 per cent. carbon), which had been hardened and then fully tempered, over which tap water was allowed to trickle for 2 years, and they do not show the slightest signs of attack. These samples were contained in a wide glass tube which was attached to a water tap ; the latter, being open slightly, allowed water to trickle continuously over the samples. Other pieces of similar steel have been immersed in slowly running water* for months without showing the least signs of attack. River and well water have also, as a general rule, no appreciable action on any normal stainless material. This may, perhaps, be best illustrated by the large number of pump rods and other fittings which have been used successfully for pumping purposes in many parts of the country. Reference may also be made to a test carried out by Dr. Newton Friend† in which a polished bar of steel containing 13·57 per cent. chromium was submerged in fresh water at Plymouth for 5 years and was then found to be in excellent condition, its surface being merely stained and slightly roughened.

Sea Water and Brine have no general action on stainless steels when the latter are completely immersed though they tend, on long exposure, to cause pitting. The tendency for pitting to be produced is less, the higher the chromium content and it is also generally less in the austenitic chromium-nickel steels than in the plain chromium steels

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* In the running water tests mentioned above, and also in the previous chapter, the samples were supported in a large glass bowl. A very slow stream of tap-water was led by a glass tube to the bottom of the bowl and was allowed to overflow from the latter into a sink. By this means the bowl was kept constantly full of water and any fine dust which might have been deposited from the atmosphere of the laboratory was automatically carried away.

† "The Deterioration of Structures in Sea Water. *Dept. of Sci. & Ind. Research, Tenth Report*, 1930.

of similar carbon and chromium contents.   Pitting is
frequently, though not always, greater if the immersion is
partial (in which case the effect will be greatest at the water
line, particularly if this be sensibly constant in position) or
intermittent, such as is produced by alternate "wet and
dry" tests; it is still more pronounced when the steel is
subjected to spray and is probably greatest if moist salt
crystals are deposited on the steel and are allowed to remain
in that condition for any length of time.

The amount of pitting produced by 6 months' exposure
to sea water is only slight even in the 12/14 per cent. chromium
steels; for example, samples of this type of material, con-
taining actually 12·1/13·3 per cent. chromium, in the hardened
and tempered condition were partly embedded in a block of
wood and the latter then fixed to a jetty on the sea coast, at
a point between high and low water marks.   The samples
were thus alternately wet and dry.   After 6 months' ex-
posure they were quite bright and practically unattacked;
only a few minute pits being formed; thus a sample weighing
150 grams and having a surface area of about 47 square
centimetres had a total loss in weight of 1 centigram.

Longer exposure, however, may produce more distinct
effects.   Thus Dr. Newton Friend* has recorded the results
of tests on bars of steel containing 13·57 per cent. chromium
which were exposed to the sea at Plymouth for 5 years.
The bars were 2 feet long, 3 inches wide and half an inch thick;
one was placed at half-tide level and the other continuously
immersed.   They were both found to be very deeply pitted,
the losses in weight being about 3·4 and 7·6 per cent. respect-
ively.   In this case, the bar completely immersed was the
worse.   It should be noted, however, that the parts of the
bars which had not suffered the localised attack still retained
their original bright polish.

Considerably less effect is produced, however, in the
more resistant types of stainless steels.   For example, bars
of stainless iron containing 16·0 and 20·4 per cent. chromium,
two of "Twoscore" (17·4 and 20·6 per cent. chromium), one
of "Anka" (15·4 per cent. chromium, 10·3 per cent. nickel) and
another of an austenitic steel containing 18·8 per cent.
chromium and 25·5 per cent. nickel) were exposed, by the

* "The Deterioration of Structures in Sea-Water." *Dept. of Sci. & Ind-
Research, Tenth Report,* 1930, p. 9.

kindness of Dr. Friend, for two years in the sea between high and low water marks at Weston-super-Mare. All these bars, which were 2 feet long and 1¼ inches diameter, retained their polished surface except for the presence of a number of very minute pits. These were most distinct in the 16 per cent. chromium iron, less distinct in the 20 per cent. chromium iron and the two " Twoscore " steels, and hardly noticeable in the two austenitic alloys.

For commercial use with sea water or brine, the hardenable high chromium steels of the " Twoscore " type or the austenitic chromium-nickel steels (e.g., " Anka," " Staybrite " or " V.2.A.") have all been satisfactorily employed. For example, valves of " Twoscore " steel have operated for months with perfect success on the hot brine circulating system of the S.S. " Adriatic."

The severely corrosive effect of sea-water spray has already been noted. Strauss and Talley* reported, as a result of a comprehensive series of spray tests on a number of steels whose chromium contents varied from 7 to 27 per cent., that no steel was completely immune from attack. Some of their results have already been quoted, see pp. 266 to 269. Their materials did not include any of the " V.2.A." type of austenitic chromium-nickel steels, but one of " Rezistal " composition (16·85 per cent. chromium ; 25·8 per cent. nickel ; 2·45 per cent. silicon) was found to behave extremely well, though it was not completely immune from attack.

The intensity of attack produced by sea water spray depends to some extent on whether the latter is continuous or intermittent. If intermittent, the salt-laden moisture deposited on the samples under test may evaporate to a sufficient extent to cause the separation of moist crystals of salt which exert an extremely corrosive effect. It is doubtful, in fact, whether any corrosion-resisting steel commercially available is entirely immune from the effects of a long continued exposure to such crystals. In a series of sea water spray tests, carried out in the author's laboratory, the samples under test were exposed to spray during 8 hours in each day and for 5 days in the week. During the remaining parts of the 5 days and also during the week-ends,

* " Stainless Steels : Their Heat Treatment and Resistance to Sea-Water Corrosion." *Proc. Amer. Soc. Steel Treat.*, Vol. XXIV, Pt. II, 1924.

the spray was cut off and the samples allowed to stand in the moisture-laden atmosphere of the spray box. Appreciable evaporation took place during these periods and, during the week-ends at least, minute crystals of salt were formed on the surfaces of the samples under test. The experiment lasted 88 days (2,150 hours), the actual spraying time being 400 hours, and under these very corrosive conditions, yielded the results given in Table LXXIV.

TABLE LXXIV.

Sea-Water Spray Tests.

No.	Analyses of steels.					Loss in weight ; grams.	Remarks.
	Carbon %	Chromium %	Nickel %	Molybdenum %	Tungsten %		
A.	0·32	12·7	0·40	—	—	0·179	Badly pitted.
B.	0·07	13·8	0·38	—	—	0·045	Pitted.
C.	0·09	17·8	0·12	—	—	0·031	,, less than B.
D.	0·08	20·7	0·23	—	—	0·006	Slightly pitted.
E.	0·08	17·0	2·15	—	—	0·002	Very slightly pitted.
F.	0·16	17·4	1·62	—	—	0·019	Slightly pitted.
G.	0·12	16·9	10·7	—	—	nil	⎫
H.	0·16	17·2	10·6	—	—	nil	⎪
J.	0·12	18·0	8·2	—	—	nil	⎬ Minute pits, just
K.	0·13	17·2	10·1	3·42	—	nil	⎪ visible.
L.	0·29	17·7	9·73	—	1·64	nil	⎭

It may be noted that each of these samples weighed approximately 65 grams and had a surface area of 25 square centimetres.

Contact Corrosion and Electrochemical Attack. It may be convenient to refer here to a type of attack which is produced under certain conditions with most, if not all, stainless steels and which, for want of a better term, may be called " contact corrosion." In the early days of these steels it was observed that if a piece of the usual " stainless " cutlery steel (containing 12 per cent. chromium or thereabouts) was immersed in a dilute solution of some salt, or even in ordinary tap water, contained in a glass beaker, corrosion was liable to occur at the points where the steel touched the glass. Covering the glass with a layer of paraffin

wax so as to eliminate contact between glass and steel did not prevent attack taking place, though it reduced to some extent the probability of it occurring.   In the same way, if a sample, suspended by string, cotton, silk or other fibre, were totally immersed in water or a salt solution, corrosion might be looked for at the points where the suspending fibre touched the steel.

It seemed unlikely that the steel could be electropositive to all these other materials and that the local corrosion could be thus due to differences of potential between the steel and the supporting material, but in order to exclude as far as possible any such potential differences, tests were made in which a sample under test was supported only by a piece of similar material.   In these tests, a short bar of the selected material was heat treated, machined or ground on all surfaces, and then cut in two, so as to produce two pieces approximately 25 mm. long and 10 mm. square.   These pieces were generally polished on all sides with 00 Fortin emery paper, but in some cases (in order to provide as uniform a surface as possible) they were polished in the manner that metal samples are prepared for microscopical observation.   One piece was then placed in a suitable receptacle and the other cross-wise over it ; in this way the samples were in contact on an area 10 mm. square on one of their longitudinal faces.

Experiments were first made with a steel containing 0·37 per cent. carbon and 11·2 per cent. chromium, i.e., of the " cutlery " type but rather higher in carbon and lower in chromium than usual.   It was found that samples of this steel, whether annealed, hardened, or hardened and tempered, if immersed in a beaker containing tap water, salt water or even recently-boiled distilled water, were invariably corroded on the contact area in less than 24 hours.   Fig. 177 shows the appearance of the contact faces of samples after 24 hours' immersion in tap water and a 3 per cent. solution of common salt respectively.

It was found that the probability of corrosion occurring on the contact face was less if the fluid, in which the specimens were immersed, was in motion.   For example, samples of the same steel placed in a dish through which a slow stream of tap water was flowing were quite unattacked after 21 days. The presence of some salts appeared to prevent attack, thus no corrosion was produced on samples immersed in dilute

Plate XL

FIG. 177.— "Contact corrosion" in steel containing 0·37 per cent. carbon and 11·2 per cent. chromium after 24 hours in tap-water (L.H.) and a 3 per cent. solution of sodium chloride (R.H.)

solutions of the following :—caustic soda, sodium carbonate, sodium bicarbonate, sodium sulphite, manganese sulphate, potassium bichromate and potassium nitrate. On the other hand, solutions of sodium chloride, sodium sulphate, potassium chloride, potassium sulphate, magnesium chloride and magnesium sulphate appeared to increase the amount of corrosion. The presence of greasy matter also prevented attack ; thus no effect was produced on samples immersed (in contact with each other) for 6 weeks in a mixture of " Philips Hydraulic Lubricant " and water.

The likelihood of corrosion occurring was found to decrease as the chromium content of the steel was increased ; thus whereas corrosion could frequently be detected at the contact surfaces of samples of the 11·2 per cent. chromium steel mentioned above after 2 hours' immersion in a 3 per cent. solution of common salt, attack was not visible on samples of stainless iron containing 14 per cent. chromium, similarly tested, after 6 weeks' immersion and was only slight after 9 weeks. Samples of " Anka " steel were quite free from corrosion after 2 months' contact in sea water.

The probability of attack occurring was also less if the contact surfaces were curved instead of flat ; thus two round bars, ¼ inch in diameter, of a 12 per cent. chromium steel were left crosswise in contact in water for several weeks without any attack being produced.

Whatever be the explanation of these peculiar corrosion features, and it seems probable that they are connected with the breakdown of the invisible protective oxide film (see page 259), this being possibly produced by differential aeration of the fluid, they furnish an explanation of some apparently mysterious cases of corrosion of stainless steel articles which have been noted from time to time. For example, a number of stainless steel knives were observed to be pitted when they were taken out of stock. The steel was found to be of suitable composition and had been satisfactorily heat treated. The pitted blades, when tested with vinegar, were quite free from the slightest stain. Investigation showed that the knives had been stored for a long period in folding cloth cases, each knife in a separate pocket, and that the cloth in all probability had been damp. Prolonged contact of metal and damp cloth at a number of points had led to the pitting of the former at these places.

A more important manifestation of the same trouble was noted in certain steam and hydraulic-fittings made of the steel. The latter has been widely used for the valves, seats, and spindles of steam valves. Resistance both to corrosion, and erosion is desirable for the first two parts and the 12/14 per cent. chromium steel, possessing these features in marked degree, has been most successful when employed for these purposes. The steel also behaved creditably at first when made into spindles but, later, complaints were received that these were pitting badly. An explanation was soon forthcoming; the earlier valves had been put into service almost immediately after they were manufactured and they were still in good condition after long periods of use. The success of these valves had naturally led both valve makers and users to stock valves, fitted with stainless steel parts, against future requirements. After assembly, such valves are almost invariably tested hydraulically, as a routine method of inspection. The testing saturates the asbestos packing with water and when the valve is subsequently put into stock for a long period, pitting is produced owing to prolonged stationary contact between steel and moist asbestos. Under such circumstances pitting is much less likely to be produced, under given conditions, with the 16/20 per cent. chromium " Twoscore " steels than with the ordinary 12/14 per cent. chromium product. Austenitic chromium-nickel steels, of similar high chromium content, are still more immune, but it is probably safe to say that no manufacturer of stainless steels, who had had any considerable experience in connection with their engineering use, would be prepared to guarantee that any form of this material would be perfectly immune from pitting if made into a spindle and left in contact with damp packing for long periods.

It seems probable that the trouble would be entirely avoided if a greasy packing were used. It may be urged, of course, that such a packing is of no advantage in a steam valve as the grease would very soon be removed from the packing by the hot steam when the valve was in use. That however is not the point : spindle corrosion is practically unknown in valves which are in use, even when these are fitted with 12/14 per cent. chromium steel ; it occurs during the time the tested valve is kept in stock and the presence. of grease in the packing would minimise very considerably

the possibility of the spindle being attacked during this period.

If packings containing graphite are used, corrosion troubles will almost certainly be accentuated, because this substance is electronegative to stainless steels. Damp graphite placed in contact with 12/14 per cent. chromium steel quickly causes electrochemical attack of the latter; action is very much slower with both the higher chromium " Twoscore " and the austenitic chromium-nickel steels and, in numerous cases, both these classes of steel have been used satisfactorily with graphite packings. At the same time, entire absence of attack cannot be guaranteed in all circumstances with these steels and particularly in the simultaneous presence of sea water. A greasy graphite packing, however, may be satisfactorily used with all these types of stainless steel; in many cases, a packing of this type would appear to be preferable, on general grounds, to one free from grease.

Many modern packings are compounded with rubber and sometimes serious trouble is caused owing to the high sulphur content of the rubber used. The author has met with some samples of packings whose sulphur content exceeded 4 per cent. of their total weight. The use of such packings should be avoided; they are liable to cause almost any type of stainless steel to corrode, particularly if, owing to a very brief vulcanising treatment, most of the sulphur in the rubber exists free.

Probably the most troublesome form of electrochemical attack which has been experienced with stainless steels is that due to contact with copper and its alloys. These metals are decidedly electronegative to the 12/14 per cent. chromium steels; hence, if they are in contact with the latter in the presence of an efficient electrolyte, corrosion of the steel may be looked for. An electrolyte is, of course, necessary for electrochemical action and this accounts for the absehce of any such action in steam equipment. For example, seats of steam valves made of 12/14 per cent. chromium steel are perfectly satisfactory even though they be screwed into bronze (or other copper alloy) valve bodies. Condensed steam also causes little or no trouble for the same reason, but saline waters act very efficiently as electrolytes and, if present at the contact surface, soon lead to the steel being selectively attacked. Fig. 178—representing a 12/14

per cent. chromium steel bolt after immersion, in contact with a bronze nut, for some time in the Manchester Ship Canal--illustrates the ravages produced by electrochemical effects due to contact with copper alloys.

A distinctly higher chromium content gives very much greater resistance to this form of attack ; e.g., samples of " Twoscore " steel have shown no signs of corrosion after 6 months' contact with bronze while immersed in sea water, conditions which frequently produce distinct attack on the lower chromium steels in a few days. A still greater degree of immunity is obtained by using the austenitic steels; in fact, when correctly heat treated, the "Anka-Staybrite-V.2.A." steels appear to resist this form of attack almost completely.

Steam. Neither saturated nor superheated steam, up to a temperature of about 650°C., has any action on stainless steel ; hence these materials have been widely used for steam fittings. In many cases, the 12/14 per cent. chromium variety is used on the score of economy and also because its range of mechanical properties and ready response to heat treatment processes renders it particularly adaptable for engineering work. The value of the steels in steam plant is enhanced by their good resistance to the erosive action of a steam jet. The comparative behaviour of the 12/14 per cent. chromium steel (0·3 per cent. carbon), ordinary steel and phosphor bronze is illustrated in Fig. 179. Small flat samples of these materials were held in a wooden frame, each specimen $\frac{1}{8}$ inch from a jet, $\frac{1}{16}$ inch in diameter, through which steam was blown at a pressure of 120 lbs. per square inch. The test was continued for 200 hours, the appearance of the samples at the end of the test being shown in Fig. 179. The stainless steel specimen, which was in the hardened condition, was practically unattacked, the only effect being a barely perceptible discoloration. On the other hand, the samples of ordinary steel and of phosphor bronze were deeply eroded where the steam jets had impinged on them.

The absence of electrochemical attack on even the 12/14 per cent. chromium steel when in contact with copper alloys in the presence of steam has already been commented on. For the purposes of testing the possible action of such alloys and also a bearing metal, small samples of a 12/14 per

Plate XLI

Fig. 178.   Corrosion of 12/14 per cent. chromium steel bolt due to contact with bronze nut.
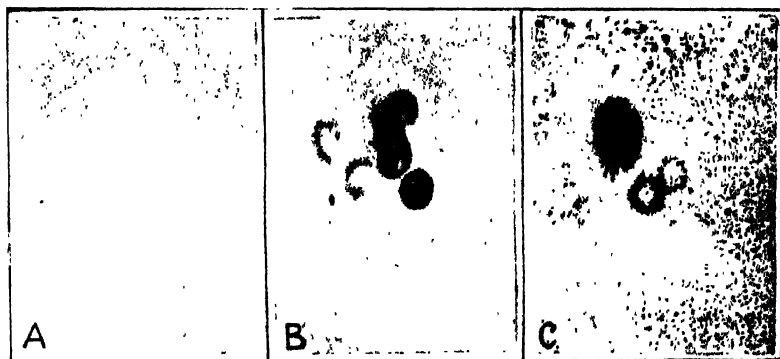
Fig. 179   Erosion tests with steam jet.   (See page 330.)
          A.   Hardened stainless steel.
          B.   Chill cast phosphor bronze
          C.   Mild steel.
     (The only effect on the stainless steel was a discoloration almost too slight to reproduce   The multiple pits in B and C are due to accidental movement of the specimens during the course of the experiment.)

cent. chromium steel were tightly embedded in pieces of
each of the following alloys* :—

.	Percentage Composition.					
	Copper.	Tin.	Zinc.	Lead.	Nickel.	Anti-mony.
Gun-metal	88	10	2	—	—	—
Copper-nickel Alloy ...	53	8·5	9	14	14	1·5
Metallic Packing ...	—	20	—	65	—	15

The duplex samples were exposed, in a steam pipe, to
the action of steam at 360°F. for a period of 3 weeks. During
each week, the boilers were working for 4 days and were
shut down during the week-ends. The samples were thus
exposed for 12 days to the action of hot steam and during
the week-ends (9 days in all) to the damp atmosphere of the
comparatively cold pipe. At the end of the test, the only
visible effect on the stainless steel samples was the
production of a dark straw temper colour. Both the gun-
metal and the nickel alloy were tinted more deeply than the
stainless steel, while the metal packing was distinctly
attacked, producing an etched surface.

As is well known, steam and ordinary steel react at a
low red heat producing hydrogen and iron oxide. The speed
of this reaction increases with temperature, but it has already
become so noticeable at 500°C. as to limit the degree of
superheating of steam to temperatures below this unless a
more resistant metal is used, e.g., for the tubes of
superheaters. The incidence of this reaction can be delayed
until considerably higher temperatures are reached if stainless
steel be substituted ; for example, no appreciable formation
of hydrogen takes place when steam is in contact with stain-
less iron (12/14 per cent. chromium) until the temperature
reaches about 650/700°C. Some experiments carried out
at Brown Bayley's Steel Works may be briefly described.
Steam at 160 lbs. per square inch pressure was superheated to
750°F. (399°C.) and then passed through the coil of tube
under test which was heated electrically to 1,000°/1,040°C.

* The duplex samples were prepared in the following manner. A hole was
drilled in a disc of the alloy and a piece of the stainless steel, machined to a driving
fit in the hole, was driven into this. By this means, metallic contact between
alloy and stainless steel was obtained.

(538°/560°C.), as indicated diagrammatically in Fig. 180. After leaving the test coil, the steam expanded through a stainless steel jet into an expansion chamber and then passed through a condensing coil, terminating in a trap where any hydrogen contained in the steam was collected and measured.
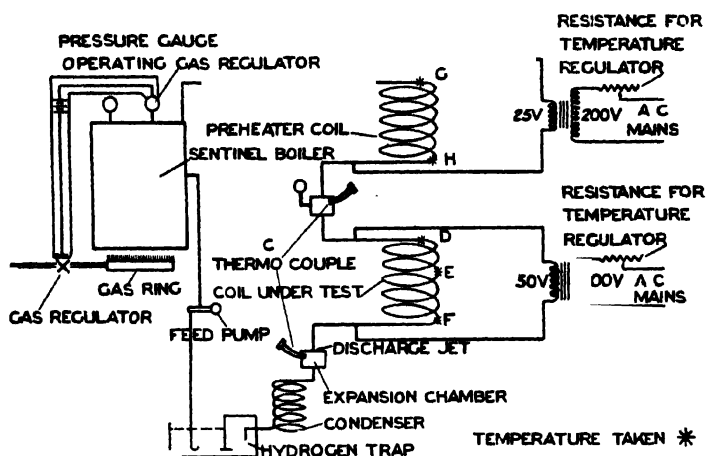
FIG. 180. Diagram of apparatus for tests with steam at high temperatures.

The steam which passed through a test coil of mild steel tube in 4 hours contained ½ a litre of hydrogen. On the other hand, when test coils of stainless iron and " Anka " steel were subsituted, no hydrogen was produced, although the experiments were continued for 223 and 1,176 hours respectively.

Aqueous Solutions of Salts. It may be doubted whether the results of laboratory experiments in which samples of stainless steel (or any other metal) are totally immersed in salt solutions, contained in beakers or other receptacles at atmospheric temperature are of any great practical value except in so far as they indicate whether attack does or does not take place and, if it does, whether immediately or slowly. The results obtained simply refer to the conditions under which the tests are carried out and will vary as these conditions vary, so much so that the relative rates of corrosion of a number of samples which were more or less attacked by a given solution might alter to a considerable extent if changes were made in the conditions

of the test, such as, for example, duration, depth under surface of liquid, method of support, or temperature.

When corrosion takes place in stainless steels under such conditions of test, it frequently starts at the point of support and often is entirely confined to that point.   In such cases, therefore, the amount of corrosion or even the presence or absence of corrosion, will depend on how a sample is supported; and conditions in which it rests against the bottom and sides of a glass beaker, or on a layer of paraffin wax, or is supported by a glass hook, or suspended by a piece of cotton or other fibre are not likely to occur in the practical application of stainless materials !   It is not intended, therefore, to give details of how particular samples of stainless steels behaved when completely immersed in aqueous solutions of various salts.   Speaking generally, it may be said that many such solutions have little or no effect on stainless material and when corrosion does take place, it proceeds very much slower than with ordinary mild steel.

Solutions of the following salts, among others, appear to have no direct action on any form of stainless steel which is completely .immersed in them.   Corrosion of the sample at the point of support, when this is below the level of the liquid, and also local pitting are apt to occur with solutions of the salts marked with asterisks ; in either case, the liability for such attack to take place, and its extent when occurring, depend on composition in much the same way as the pitting produced by sea-water.

Alkaline Bicarbonates.	Copper Sulphate.
„ Bichromates	Ferric Nitrate.
„ Carbonates.	„ Sulphate.
„ Cyanides	Ferrous Sulphate.
„ Nitrates	Lead Acetate
„ Nitrites.	*Magnesium Chloride.
„ Permanganates.	* „ Sulphate.
„ Phosphates.	Manganese Sulphate.
„ Sulphites.	Potassium Chlorate.
Ammomium Oxalate.	„ Chloride.
„ Persulphate.	„ Ferricyanide.
„ Phosphate.	*Sodium Chloride.
Copper Acetate.	„ Sulphide.
„ Nitrate.	

Dilute solutions (e.g. 5 per cent.) of ammonium sulphate, sodium sulphate and potassium sulphate have also no action on stainless steels but stronger solutions of these salts, e.g. 25 per cent.—have a slight action on the 12/14 per cent. chromium steels though they have no effect on the austenitic alloys. Aluminium sulphate and potash or ammonia alum have a rather more pronounced effect on the 12/14 per cent. chromium steels, some action being produced even with 5 per cent. solutions, but again they have no action on the austenitic alloys. Solutions of ammonium chloride have generally no effect on the high chromium " Twoscore," or the austenitic steels but they are likely to cause pitting in the lower (12/14 per cent.) chromium steels and irons.

On the other hand, solutions of ferric chloride, copper chloride and mercuric chloride* will attack any form of stainless steel, the attack being general with stronger solutions and often local, leading to pitting, with those more dilute. Solutions of bleaching powder, unless very dilute, are also likely to produce pitting in any form of stainless steel.

Ability in a metal to withstand cold solutions of various salts, when completely immersed in the latter, is not of very great interest to the chemical manufacturer in search of resistant metals for the construction of plant. His solutions are generally hot and he frequently wishes to concentrate them. There is likely to be a liquid-air interface in some part of the apparatus and experiment shows that when samples of stainless steel are only partially immersed in various salt solutions—particularly of chlorides and sulphates, —attack is more likely to occur at the level of the liquid then elsewhere, especially if the location of this level is fairly constant. Such attack takes the form of pitting and, generally speaking, is less likely to occur in the austenitic chromium-nickel steels than in nickel-free steels of similar

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* A very dilute solution of mercuric chloride (1 : 1000) is occasionally used as an antiseptic. For example, instruments may be immersed for a short time in such a solution immediately before being used surgically. No appreciable effect would thereby be produced on even the 12/14 per cent. chromium steels, and instruments made of such steels could quite safely be sterilised in this manner. If, however, the instruments were left for a long time in the solution, or if after being sterilised they were allowed to dry and then put away for some time, with minute particles of mercuric chloride adhering to them, it is possible that minute pits would be formed on the steel surface, an undesirable feature in a surgical instrument. A similar effect would also be most likely produced if the mercuric chloride solution were used at boiling point and the instruments left in, e.g., for fifteen or twenty minutes.

chromium content. Probably the most severely corrosive conditions, with any given salt, are to be met with in evaporators or similar plant in which hot moist crystals of the salt are formed and are deposited on various parts of the metal equipment ; where this occurs, pitting may be produced even with salts (especially if these be chlorides or sulphates) which normally have no action on the particular form of stainless steel used.·
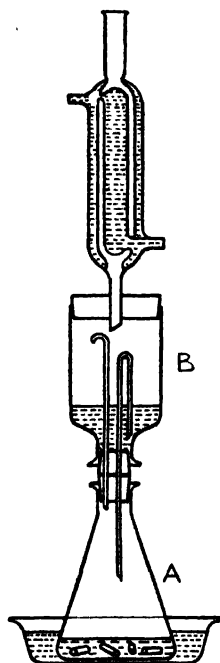
FIG. 181.   Apparatus for testing with boiling salt solutions ;   variable concentration.

A useful form of test which gives information as to the resistance of the steels to boiling solutions of a salt, over a wide range of concentration, may be obtained by means of the apparatus shown in Fig. 181, which also has the merit of requiring little attention during the progress of a test.   The samples are placed in the flask A together with a sufficient amount of a dilute solution of the salt in question to cover them completely.   On boiling the solution in A, the steam is condensed and runs back into the receiver B ;

when sufficient has collected in the latter, the syphon functions and returns the condensate· to A. After a preliminary adjustment of the amount and strength of the solution used and also of the capacity of the reservoir ·B before the liquid contained therein syphons back into A, the samples under test may be made to pass through a cycle of corrosive conditions from a dilute solution of the salt used to a moist paste of the hot crystals. · By controlling the rate at which evaporation takes place in A, this cycle may be made to occur quickly or slowly. A summary of the results obtained by testing various types of stainless steels in an apparatus of this kind, using different salts, are given in Table LXXV. As a rule the cycle of changes occupied about three hours and each test was continued for seven days.

A still more severe form of test, and one which reproduces reasonably well the conditions obtaining in many evaporators, may be devised somewhat on the following lines. The sample, preferably in the form of rod or strip four inches or so long, is suspended vertically in a tall bottle or jar, eight or ten inches high, so that its lowest point is about two inches above the bottom of the jar. A sufficient amount of a dilute solution of the salt is then poured into the jar so as to cover the sample completely. The jar is then placed in a water · bath (preferably fitted with an automatically controlled water supply) whose temperature is maintained at about 80° or 90° C. The sólution in the jar gradually evaporates and this is allowed to continue until the liquid level falls below the sample. The jar is then filled up again with the solution and the process repeated until the fluid in the jar becomes so concentrated that crystals of the salt deposit freely on the sample and the bottom and sides of the jar as evaporation proceeds. The process is then continued by filling up with distilled water instead of salt solution. In a test of this description, the sample is exposed to all strengths of the salt solution and also to a deposit of the hot, moist crystals. The test may with advantage be continued for· three to six months. An inspection of the sample at the end of that time will give a very reliable indication of the likely behaviour of the steel in practice.

Tests made under these conditions showed that high chromium stainless iron (16/20 per cent. chromium) and the

TABLE LXXV.

Action of Boiling Salt Solutions (varying concentration, see page 335).

Steels used.	Carbon %	Chromium %	Nickel %	Molybdenum %
A.	0·09	13·5	0·30	—
B.	0·07	15·7	0·16	—
C.	0·12	14·9	10·7	—
D.	0·18	20·2	8·8	—
E.	0·13	17·2	10·1	3·42

Salt.	Steel.	Loss in weight (grams per sq. m. per hour).	Appearance of Sample.
Alum (Potash) ...	A	258	Badly attacked.
	B	4·7	Attacked.
	C	0·2	Stained black.
	D	8·0	Attacked.
	E	0·13	Stained black.
Alum (Ammonia) ..	A	70	Badly attacked.
	B	6·6	Attacked.
	C	0·6	Roughened ; small pits.
	D	3·05	Attacked.
	E	0·08	Slightly roughened.
Aluminium Sulphate..	A	32·9	Badly attacked.
	B	6·8	Attacked.
	C	3·4	Attacked.
	D	20·2	Badly attacked.
	E	0·2	Etched light grey.
Barium Chloride ..	A, B	nil	A few minute pits on each.
	C, D, E	nil	No attack.
Calcium Chloride ..	A, B, D	nil	A few minute pits on each.
	C, E	nil	No attack.
Copper Sulphate ...	A	0·09	Blackened
	B	0·02	Lightly etched
	C, D, E	nil	No attack.
Ferric Sulphate ...	A	25·3	Badly attacked.
	B, C	nil	Slightly stained.
	D	0·21	Etched.
	E	nil	No visible effect
Ferrous Sulphate ...	A	1·73	Blackened and roughened.
	B	0·03	Stained.
	C, D, E	nil	Slightly stained.
Potassium Meta-bisulphate	A	0·02	Blackened.
	B, D	0·005	} Slightly stained.
	C, E	nil	
Potassium Nitrate	A, B, C, D, E	nil	No attack.
Sodium Acetate	A, B, C, D, E	nil	No attack.
Sodium Carbonate	A, B, C, D, E	nil	No attack.
Sodium Chloride	A	No weighable loss	Slight attack where in contact with the glass flask.
	B, C, D, E	nil	Very slightly stained
Sodium Nitrate	A, B, C, D E	nil	No attack.
Sodium Nitrite	A, B, C, D, E	nil	No attack.
Sodium Sulphate	A, B, C, D, E	nil	No attack.

austenitic steels of the " Anka-Staybrite-V.2.A. " type were satisfactory with, for example, solutions of caustic soda and sodium sulphide, but that pitting was produced in both classes of material (even when containing up to 20/21 per cent. chromium) by solutions of ammonium sulphate, ammonium chloride, magnesium chloride or sodium chloride. The pitting was generally less in the case of the austenitic steel than the stainless iron ; it was also reduced in amount by the addition of copper or molybdenum to the austenitic chromium-nickel steels, but no type of steel was found to be entirely immune from pitting after testing in these four salt solutions in the manner described for a period of six to eight months.

It is not to be inferred that the amount of pitting referred to above is sufficiently great to prohibit the use of the various steels in practice. This is far from being the case ; actually various types of these steels are being used successfully for dealing with one or other of the salts mentioned. For example, a considerable amount of the austenitic type of steel has been employed in the construction of plant for the manufacture of ammonium sulphate ; similarly, solutions of sodium chloride are being satisfactorily handled either by these steels or by the irons or hardenable steels containing 16/20 per cent. chromium, but it should be realised that perfect immunity from attack during prolonged use cannot be guaranteed.

In the case of ammonium sulphate, matters are some-what complicated by the tendency of this salt to dissociate when its solutions are boiled, as a result of which the latter become slightly acid. For this reason, the austenitic chromium-nickel steels are preferable for handling this salt as they have a greater degree of resistance to very dilute solutions of sulphuric acid than the plain chromium irons and steels.

Ammonia and Alkalies. Solutions of ammonia of all concentrations and at all temperatures appear to have no action on any form of stainless steel ; the latter also retain their lustre indefinitely when exposed to damp atmospheres containing ammonia.

Caustic alkalies have no action on stainless steels at ordinary temperatures. At higher temperatures--e.g., 80/110° C.—dilute solutions have also no effect on any

stainless steel but the effects produced with stronger solutions
—e.g., 30 per cent. or over—depend on temperature, con-
centration and the type of steel used.   Thus the 12/14 per
cent. chromium steels are attacked slightly by a 30 per cent.
solution at 100/110° C. and more rapidly by a 50 per cent.
solution at the same temperature.   In both cases the rate of
attack is less on a stainless iron containing 15/16 per cent.
chromium and is either nil or negligible on the austenitic
steels.   Some values obtained experimentally are given in
Table LXXVI.

TABLE LXXVI.

Action of Caustic Soda on Stainless Steels.

Composition of Steel.			Temperature of Test.	Strength of Solution.		
Carbon %	Chromium %	Nickel %		5%	30%	50%
0·19	12·0	0·21	100/110° C.	nil	0·15	1·03
0·08	15·4	0·30	,,	nil	0·11	0·59
0·10	15·4	11·4	,,	nil	nil	0·04
0·13	15·9	11·0	Boiling ...	—	—	3·3*
0·16	17·2	10·6	,,	—	—	2·8*
0·18	20·2	8·8	,,	—	—	2·8*

* The solution was concentrated to about two-thirds of its original volume
during the test.

It will be noted that a 50 per cent. (or rather stronger)
solution has a distinct action at boiling-point on the austenitic
steels.   Further concentration of such solutions leads to
a still greater attack, the effect being quite marked with,
e.g., a mixture of 70 per cent. caustic soda and 30 per cent.
water at a temperature of 300° C. or so.

Vinegar and Fruit Juices.   The use of stainless steel
for cutlery purposes has been the cause of the very general
use of vinegar as a kind of test reagent for stainless material,
and its effects, or lack of them, have been referred to several
times in the preceding pages.

Commercial vinegars vary to some extent in their
corrosive action.   The tests which are quoted in this book
were obtained by the use of pure malt vinegar, of good
commercial quality, containing four to five per cent. of

acetic acid. Some commercial products, however, contain distinct amounts of sulphuric acid; such "vinegars" have a distinctly greater action on stainless material (particularly the 12/14 per cent. chromium steels and irons) than the pure article.

The vinegar test with stainless steel is most usually carried out by placing a drop of the vinegar on a polished surface of the steel to be tested and allowing the drop to dry naturally; generally the sample is left over-night undisturbed. After the dried remains of the vinegar have been removed by washing, the surface of the steel is examined for any signs of a stain; such a stain, when produced, generally takes the form of a grey mark on the polished surface, the vinegar having then an etching action. The " spot " test described above is a more severe test than that obtained by immersing the sample in vinegar for twelve or twenty-four hours.

Stainless steel containing about nine per cent. of chromium and upwards and with the ordinary carbon content for cutlery, i.e., about 0·8 to 0·4 per cent., when suitably hardened is entirely unaffected by the vinegar spot test. The hardening temperature required to produce stainlessness will be in the neighbourhood of 1,000° C. when the chromium content is about 9 per cent. but falls as the percentage of chromium rises. On tempering such suitably hardened material, no appreciable effect on the resistance to the vinegar test is produced up to a temperature of about 500° C.; after tempering at still higher temperatures, however, it will probably stain unless the chromium content exceeds about 18 per cent. in the case of steel containing 0·3/0·4 per cent. carbon. The amount of chromium required, however, decreases with carbon content so that 10/11 per cent. is sufficient for stainless irons. A similar content also suffices for the austenitic chromium-nickel steels.

The effect of varying chromium content on the resistance to staining of steels of cutlery temper is illustrated in Fig. 182, in which are shown the results of testing specimens of such material after suitable hardening followed by tempering at the temperatures indicated.

When the steel is in the annealed condition a still greater amount of chromium is required (for any given carbon

Plate XLII
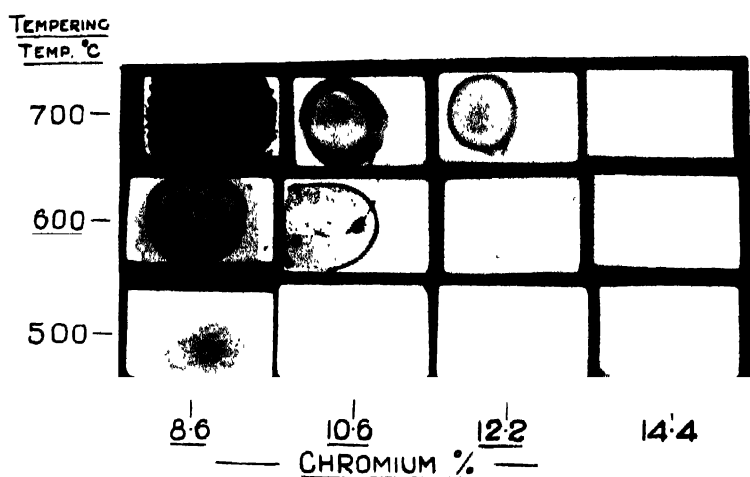
Fig. 182. Effect of chromium content on the resistance to staining, by vinegar, of stainless steels of cutlery temper, after hardening and then tempering as indicated.

content) in order to induce stainlessness; an example of this was given on page 275.

The use of vinegar as a test reagent for steel for cutlery purposes and for finished stainless cutlery is justified from the fact that vinegar is probably one of the most corrosive materials which such cutlery will have to resist in its ordinary use. The use of vinegar as a test for similar types of materials which are to be used for purposes other than cutlery, however, has not the same justification and although it has advantages in indicating in a general way the combined effect of varying composition and heat treatment, its indications do not determine whether or not a given sample will corrode when exposed to other media, e.g., ordinary tap water. For example, a drastically annealed sample of steel containing 0·32 per cent. carbon and 12·2 per cent. chromium, which stained badly when tested with vinegar in the manner described above, was immersed in tap-water for ten months without showing the least sign of attack.

Although the 12/14 per cent. chromium steel used for cutlery purposes is sufficiently immune from the attack of vinegar to function adequately for table use, it is attacked very slightly by hot vinegar. The amount of attack so produced, while being so slight as to have no noticeable effect on the steel itself, is sufficient to cause trouble if the latter be employed for the construction of plant used for the manufacture of sauces and pickles. The minute traces of iron dissolved from the steel affect quite noticeably the colour of the pickle. This trouble is entirely avoided, however, by using the higher chromium materials (such as the " Twoscore " steels or the high chromium irons) or the austenitic alloys of the " Anka-Staybrite " type.

Fruit juices in general have an effect on stainless steel similar to that of vinegar, although the degree of their corrosive power probably varies to some extent.

It is interesting to note that the acids found in vinegar and fruit juices, when used in the form of pure solutions, have generally a distinctly greater effect on 12/14 per cent. chromium steel than the corresponding natural juices. Thus, as will be seen later, a solution of pure acetic acid in water, of the same strength as that in vinegar, has a much greater effect than the latter on these steels; similarly, although lemon juice does not attack a stainless steel knife blade,

a solution of pure citric acid of the same strength exerts a distinct though slow corrosive action on the same metal.

The reason for the difference between the effects of vinegar or natural juices as compared with the pure acids contained in them lies, in all probability, in the fact that the natural products contain organic compounds in colloidal form. Such colloidal solutions have been found to exert a retarding action on the attack of other metals under diverse conditions; for example, very dilute solutions of starch or of egg albumen, in both of which the organic matter is in a colloidal state, corrode ordinary steel much more slowly than does water free from these colloids. This retarding action increases with the amount of colloid present and, as Dr. Friend has pointed out,* it has a very considerable practical importance; thus most culinary operations deal with substances more or less colloidal in character and these, by passing into the water used in such operations, retard considerably the corrosion of the cooking utensils. The noteworthy point, however, in connection with stainless cutlery is not so much the fact that retardation of corrosion occurs, but that this retardation is sufficient to prevent entirely the action of the natural juices on the stainless material when the latter has been suitably heat treated.

Nitric Acid. It is no exaggeration to say that the greatest chemical use of stainless steels has been in connection with the nitric acid industry; when containing a sufficient amount of chromium, they possess very good resistance to the attack of all concentrations of nitric acid and, as a consequence, hundreds of tons of one form or another of the steel have been used in the construction of plant for the manufacture and handling of this acid.

All types of stainless steel do not behave equally well with the acid, however, nor is the degree of resistance possessed by particular steels entirely unaffected by variations in their structural condition; hence the effects produced by these two variables—composition and treatment—on the response of the steels to nitric acid of various concentrations and at different temperatures merit a detailed consideration.

* " The Corrosion of Iron," J. N. Friend. Carnegie Sohol. Mem. (Iron and Steel Inst.), 1922. p. 144.

It is common knowledge that dilute solutions of nitric acid (e.g., 5 or 10 per cent.) have a marked attack on ordinary mild steel and that as the concentration of the acid increases, its rate of attack rises rapidly, reaching a maximum when the solution contains 30/35 per cent. of the acid and has a specific gravity of about 1·20 ; the action is then violent. Increasing the acid strength still further (e.g., to a specific gravity of 1·3/1·35) causes the rate of attack to decrease rapidly owing to passivity effects and the ordinary commercial concentrated acid (S.G. 1·42) has practically no action on the steel at atmospheric temperature.

The addition of a considerable amount of chromium to steel results in the range of acid concentration producing passivity effects being very considerably extended. For example, the maximum rate of attack on steel containing 12 per cent. chromium and 0·3 per cent. carbon occurs with acid of about normal strength, the results obtained on such a steel being set out in Table LXXVII together with others given under comparable test conditions by ordinary mild steel.

Raising the temperature of the acid to 80°/85° C. increases very considerably the rate of attack of the very dilute acid

TABLE LXXVII.

Rate of Attack of Nitric Acid on Stainless Steel and Ordinary Mild Steel.

Mark.	Carbon %	Chromium %
A	0·32	12·2
B	0·35	nil

Strength of Acid.	Rate of attack . grams per sq. m per hour.					
	15° C.		80° C.		Boiling.	
	A.	B.	A.	B.	A.	B.
N/10	4·0	6·8	51	—	380	—
N/5	6·5	17·4	87	—	720	—
N/2	11·1	85·0	151	—	935	—
N	15·3	221	55	800	800	5,500
2N	—	467	2·4	860	86	10,000
5N	0·1	6,000	0·8	—	27	—
S.G. 1·42	nil	0·5	1·8	360	52	15,000

on such a stainless steel but has much less effect when the acid strength is between N and 5N. At boiling point, the acid has a still greater effect on the steel at all concentrations, as will be seen from Table LXXVII.

It will also be noted that the passivity, which is so marked a feature of mild steel when immersed in concentrated nitric acid, does not persist when the latter is heated ; the action of boiling acid of specific gravity 1·42 is extremely rapid. Stainless steels are by no means immune under the latter conditions and, as will be seen presently, even alloys of very high chromium content are attacked, though only at a slow rate.
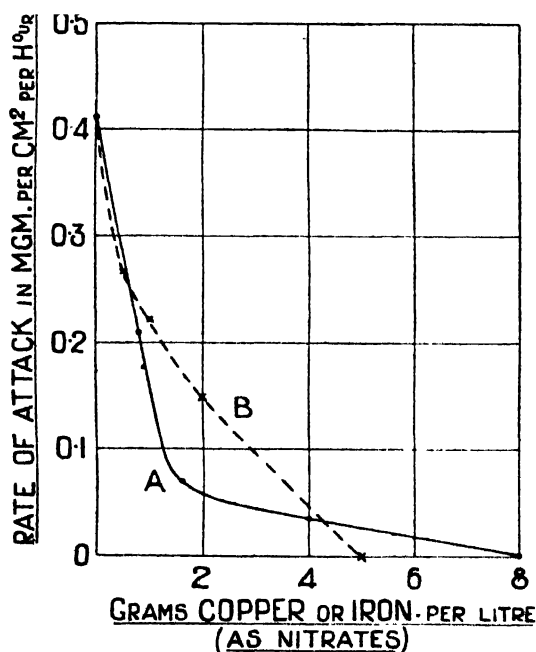
Fig. 183. Effect of copper nitrate and ferric nitrate on the rate of attack of normal nitric acid on stainless steel.
Curve A.   Copper nitrate.
,,   B.   Ferric nitrate.

Passivity effects are also by no means entirely absent even in the case of the very dilute acid and, as a result, the action of nitric acid on stainless steels has a number of interesting features. As these have a very considerable influence on the results which may be obtained from corrosion

tests, it will be useful to consider them in some detail before proceeding to the question of rate of attack in relation to composition and treatment of the steel.

Observation of a sample of a 12 per cent. chromium steel, placed in acid of normal strength, or thereabouts, will show that the rate of attack of the acid apparently gets slower and slower as time goes on ; eventually action may cease altogether. It seems very probable that this effect is due, at least in part, to the ferric nitrate which is one of the products of the attack of nitric acid on the steel. If small amounts of this salt are added to the acid, before the steel is placed in it, the initial rate of attack on the latter is greatly retarded and if sufficient of the nitrate is present, the acid no longer has any action on the steel. The results of an experiment with a steel containing 0·3 per cent. carbon and 12·6 per cent. chromium are plotted in curve B in Fig. 188, and from this it will be seen that the presence of 5 grams of iron per litre (equivalent to 21·6 grams of ferric nitrate) was sufficient, in this case, to prevent entirely the action of the acid on the steel.

It may be mentioned that copper nitrate has a precisely similar action ; curve A in Fig. 183 gives the results of tests carried out with this salt in a similar manner to those with ferric nitrate.

As ferric nitrate is formed when stainless steel is attacked by nitric acid, it follows that the results of laboratory tests on the effect of this acid on these steels will depend very largely on the manner in which the tests are carried out, such factors as bulk of acid used and duration of attack being of special importance. The extent to which results are influenced may be judged by the figures in Table LXXVIII. These relate to experiments in which a number of similar samples were tested for various times under otherwise similar conditions. For the results given in column A, samples of the steel were placed each in a relatively small bulk of acid (40 c.c.) and action had practically ceased at the end of twenty-four hours. The figures in column B relate to tests on similar samples placed in a very much larger bulk of acid (5 litres) and here the effects of time are not nearly so marked. A distinct retardation with time has also been noted in the rate of attack of N/5 acid at 80° C. on stainless iron containing 12·7 per cent. chromium.

Table LXXVIII.

Attack of Normal Nitric Acid on Stainless Steel.

	Carbon %	Chromium %	
	0·32	12·2	

Duration of Attack.	Mean rate of attack : grams per sq. m. per hour.	
	A. Each sample in 40 c.c. of acid.	B. Samples suspended in 5 litres of acid.
3 hours	15·1	28·5
6 ,,	11·2	36·7
24 ,,	2·8	20·5
72 ,,	0·9	14·0

It follows from these results that comparative tests as to the rate of attack of nitric acid on different steels should always be carried out under identical conditions, particularly as regards size of sample, bulk of acid and duration of test, otherwise the results may be entirely misleading. Also, laboratory tests of a relatively short duration are to be preferred to those occupying a longer time (unless special arrangements are made to renew the acid repeatedly), as the former are likely to give values more nearly approaching those realised in practice where the acid in contact with the metal is constantly changing.

The passive state produced by long continued action of a small bulk of acid is retained if the sample of steel is removed from the acid, well washed and dried, and then placed in fresh acid. The passivity is also retained by the dry sample for long periods. For example, samples of a 12·2 per cent. chromium steel which had become passive ,owing to three days immersion in normal nitric acid and were then washed and dried, were found to be still completely passive to fresh acid of the same strength after they had been kept for seven weeks.

Passivity is also produced if samples are taken out of the acid during the first few hours of immersion, while attack is still progressing, and washed and dried. If they are then immediately put back into acid, no further action takes place. If such samples are allowed to remain

dry, however, they lose their passivity during the course of a few hours. The passivity is not affected if the samples, on taking out of the nitric acid, are rubbed with cotton wool during washing.

The passivity produced in stainless steels by the action of nitric acid also retards, and may altogether prevent, the subsequent attack of dilute sulphuric or hydrochloric acids on the steel. An example of this action in the case of "Anka" steel has already been noted (see page 260); in this case dilute sulphuric acid had no action on the passive sample. The effects are less permanent in the case of the plain chromium steels, probably owing to the latter being more readily attacked by hydrochloric and sulphuric acids than the austenitic steels. For example, samples of a 12 per cent. chromium steel made passive by the action of nitric acid were placed in 5 per cent. sulphuric acid and were only very slowly attacked at first; the rate of attack, however, gradually increased and at the end of three or four hours the samples were being attacked at the normal rate. With 10 per cent. hydrochloric acid, passivity similarly disappeared in about two hours.

The effect of varying chromium content on the rate of attack of nitric acid has been studied by several investigators. Monnartz's results,* on alloys containing up to 20 per cent. chromium, may be summarised as follows :—

(1) In the case of alloys containing up to 4 per cent. chromium, resistance to dilute nitric acid diminishes as the chromium content increases. On the other hand, resistance to attack by the concentrated acid becomes greater.

(2) Resistance to dilute nitric acid increases very rapidly as the content of chromium rises from 4 to 14 per cent.

(3) As the chromium content rises from 14 to 20 per cent. the resistance to dilute acid continues to increase, but only slowly.

Guertler and W. Ackermann† came to the conclusion that complete passivity occurred in the iron-chromium alloys when the ratio of chromium to iron atoms was greater than 1 : 8 (i.e., when the chromium exceeded 11·74 per cent.) thus

* *Metallurgie,* Vol. VIII, pp. 161-176, 193-201.
† *Zeit. für. Metallk.,* Vol. XX, 1928, p. 269.

following Tammann's[*] theory that the susceptibility to chemical attack of binary solid solutions of metals changes abruptly at certain values of the composition, these critical values being found when the atomic proportions of one of the metals amounted to one-eighth of the whole or to some integral multiple of that fraction. Guertler and Ackermann, however, tested their alloys with nitric acid of two strengths
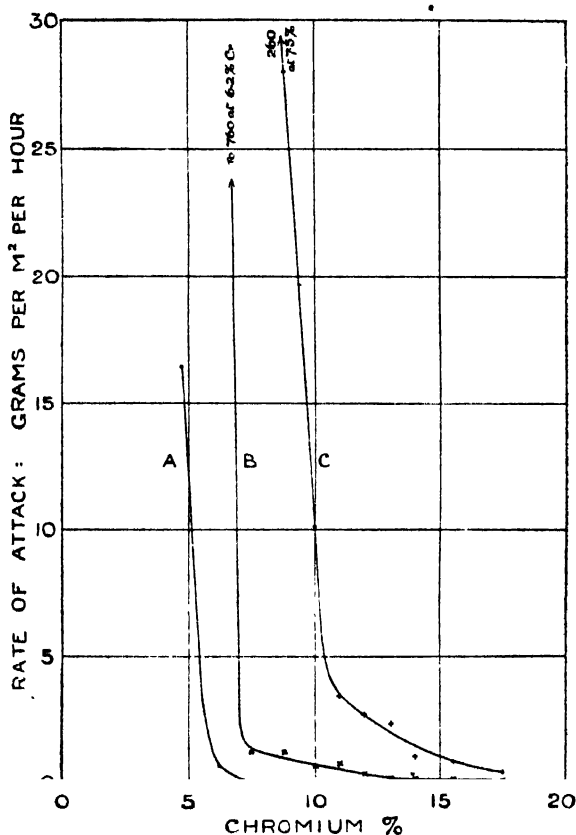
Fig. 184. Rate of attack of nitric acid (S.G. 1·20) on stainless irons.
Curve A. 15° C.
„ B. 80° C.
„ C. Boiling.

only (S.G. 1·005 = 1·0 per cent.; S.G. 1·12 = 20·23 per cent.) and all their tests were done at atmospheric temperature.

* Zeit. Anorg. Chem , Vol. CVII, 1919, p. 1.

Results obtained by the author on a series of low carbon iron-chromium alloys indicate that the amount of chromium required to induce passivity varies considerably with strength of acid and temperature. This is evident from the results given in Table LXXIX. The values obtained with acid of S.G. 1·20 are particularly interesting and the dependence on temperature is strikingly evident in Fig. 184, wherein the data relating to this particular acid are plotted.

TABLE LXXIX.

Effect of Chromium Content on the Rate of Attack of Nitric Acid on Steel.

Rates of attack in grams per sq. m. per hour ; duration of each test, 24 hours.

Composition of Alloy.		Strength of Acid and Temperature.									
		N/10.		N.			S.G. 120.			S.G. 1:42.	
Carbon %	Chromium %	15° C.	Boiling	15° C.	80° C.	Boiling	15° C.	80° C.	Boiling	15° C.	40° C.
0·16	nil	12·0	—	54	—	—	12,500	—	—	1·01	5·62
0·14	4·72	11·5	—	64	—	—	16·4	—	—	0·07	0·26
0·12	6·2	13·6	—	62	—	—	0·64	755	—	0·07	0·16
0·09	7·5	11·2	—	33	37	—	0·05	1·18	257	0·04	0·20
0·18	8·8	11·4	—	49	31	263	0·03	1·23	27·9	0·04	0·13
0·16	10·0	6·4	40·3	11·3	18	24	0·02	0·59	10·1	0·04	0·06
0·15	10·9	2·7	25·1	3·1	3·6	4·0	nil	0·72	10·5	nil	0·21
0·09	12·0	1·18	7·5	1·15	0·8	1·41	nil	0·33	2·7	0·07	0·18
0·14	13·1	1·16	0·8	0·05	0·07	0·07	nil	0·11	2·3	nil	0·25
0·09	14·0	0·26	0·6	0·03	nil	nil	nil	0·09	0·95	nil	0·09
0·10	15·5	nil	nil	nil	nil	nil	nil	0·10	0·80	nil	0·09
0·13	17·5	nil	nil	nil	nil	nil	nil	0·07	0·35	nil	nil

Pilling and Ackermann* tested an extensive series of chromium and nickel-chromium steels and found that the limit of attack in nitric acid did not occur at a fixed chromium content but varied through a wide range continuously with the acid concentration. The actual values obtained by these two investigators for the corrosion rates of chromium and chromium-nickel steels in cold 5 per cent. nitric are much higher than those found by any other investigator with whose work the author is acquainted. For example, their rates of attack on stainless irons containing

* " Resistance of Iron-Nickel-Chromium Alloys to Corrosion by Acids." N. B. Pilling and D. E. Ackermann. *A.I.M.M.E. Tech. Pub. No.* 174, 1929.

15 and 18 per cent. chromium are equivalent to 29·0 and 2·25 grams per square metre per hour respectively ; the former rate of attack would reduce a ½-in. plate (if attacked on one side only) to half its thickness in about five and a half weeks, the latter in rather less than seventeen months. As the rate of attack of acid of this strength increases with temperature, it is obvious that the figures obtained by Pilling and Ackermann can have little relation to actual practice otherwise the nitric acid plants made of steel containing 16/18 per cent. chromium and in use in this country and the United States of America would have been in a parlous condition long ere this.
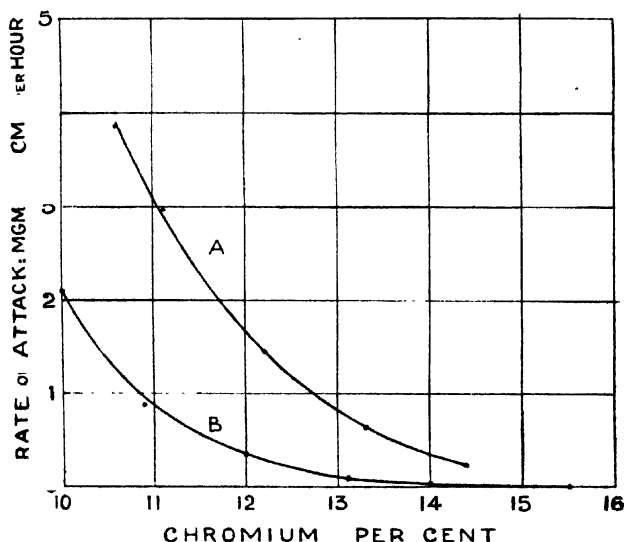
FIG. 185. Effect of chromium content on the rate of attack of normal nitric acid on stainless steel.

Curve A.   Steels with 0·31/0·33 per cent. carbon.

   ,,   B.   ,,   ,,   0·09/0·16 ,,   ,,   ,,

(N.B.—0·1 mgm. per cm² per hour = 1 gram per. sq. m. per hour.)

The results given in Table LXXIX and Fig. 184 indicate that a minimum of 15/16 per cent. chromium is necessary in a stainless iron in order to give the latter a reasonable resistance to nitric acid. As the protective action of chromium is likely to be exerted only when it is actually

dissolved in the iron and not when it is present as structurally free particles of carbide, one would expect to find that the addition of carbon to a high chromium steel lowers the latter's resistance to nitric acid. That this is the case is evident from the results plotted in Fig. 185. Roughly speaking, the addition of 0·1 per cent. carbon necessitates the chromium content being raised rather more than one per cent. in order that corrosion resistance be not impaired.

It was shown in the previous chapter that the addition of nickel to a high chromium steel did not increase the latter's resistance to nitric acid. If, however, sufficient nickel is present to produce an austenitic steel—such as " Anka," " Staybrite," " V.2.A." and the like—a slight beneficial effect is indirectly produced. The austenitic steels are normally used in a heat treated condition which produces a homogeneous structure of austenite. In this condition, the whole of the chromium in the steel is able to exert its protective effect. In the stainless irons, on the other hand, about 1 per cent. chromium is present as a free carbide ; hence the minimum percentage of chromium required to produce adequate resistance to nitric acid in austenitic steels is somewhat less than in stainless irons.

TABLE LXXX.

Action of Boiling Nitric Acid on Stainless Steels.

(Rates of attack in grams per sq. m. per hour).

Composition of Steel.						Concentration of Acid.						
Carbon %	Silicon %	Chromium %	Nickel %	Molybdenum %	Tungsten %	0·63% N/10.	3·15% N/2.	6·3% N.	12·6% 2N.	31·5% 5N.	69·8% S.G. 1·42	95% S.G. 1·50
0·09	0·28	12·7	0·60	—	—	5·1	11·8	37·5	10·9	0·9	4·25	3·0
0·08	0·24	15·4	0·30	—	—	0·3	0·3	0·4	0·4	0·6	1·7	0·8
0·07	0·23	17·2	0·24	—	—	nil	nil	nil	nil	nil	0·5	0·9
0·14	0·45	22·8	0·08	—	—	nil	nil	nil	nil	nil	0·5	0·8
0·10	0·37	24·4	0·37	—	—	—	—	—	—	—	0·42	—
0·24	0·63	28·1	0·30	—	—	—	—	—	—	—	0·30	—
0·12	0·16	14·9	10·7	—	—	nil	nil	0·004	0·026	0·07	0·68	0·64
0·10	0·38	16·6	10·2	—	—	nil	nil	nil	nil	nil	0·53	0·62
0·12	0·30	18·0	8·2	—	—	nil	nil	nil	nil	nil	0·55	0·41
0·13	0·30	20·1	9·9	—	—	nil	nil	nil	nil	nil	0·48	0·20
0·14	2·10	22·3	11·1	—	—	nil	nil	nil	nil	nil	0·50	0·22
0·15	0·5	24·2	11·2	—	—	nil	nil	nil	nil	nil	0·15	0·40
0·13	0·45	17·9	18·6	—	—	nil	nil	nil	nil	nil	0·24	0·37
0·13	2·65	17·1	25·4	—	—	2·38	1·28	0·29	0·20	0·40	2·64	0·5
0·13	2·68	17·0	25·2	—	3·3	2·29	2·18	0·50	0·20	0·40	2·86	0·3
0·13	0·54	17·2	10·1	3·42	—	nil	nil	nil	nil	nil	1·40	0·4
0·13	0·44	11·5	35·4	—	—	7·49	16·5	1·78	1·10	0·20	2·16	0·82

Table LXXX gives data relating to the behaviour of some typical irons and steels with nitric acid of different concentrations. A noticeable feature of these results is the increase in the rate of attack of the boiling acid when its concentration exceeds about 50 per cent. The most rapid action appears to be obtained with acid of 65/70 per cent. strength, probably because the temperature of the boiling point is here at a maximum; and as will be seen from the data given, acid of this concentration has a distinct action on steel with as high a chromium content as 28 per cent.

Data recently published by Huey* and given in Table LXXXI show how the rate of attack of this acid is influenced by temperature.

TABLE LXXXI

Action of 65% Nitric Acid on Stainless Irons

(Rates of attack in grams per sq. m. per hour.)

Carbon %	Chromium %	Temperature.			
		15° C.	90° C.	110° C.	124° C. (B.P.)
0·09	12·4	0·010	0·51	1·47	8·7
0·09	15·8	0·004	0·13	0·37	1·81
0·08	18·5	Nil	0·08	0·17	0·73

Summing up, it is evident that stainless irons containing 16 per cent. chromium or over, and austenitic steels containing 15 per cent. or more chromium, together with 7/12 per cent. nickel, resist almost completely the attack of nitric acid up to about 50 per cent. strength at all temperatures up to boiling point and of acid of higher concentration than about 50 per cent. at all temperatures up to about 90°C. At temperatures above about 100°C., the steels are attacked by the latter strengths of acid at rates which may reach 0·5/1·0 grams per square metre per hour at boiling point. The results also indicate that nickel up to about 18 per cent. has no ill effect but that if the content of this metal reaches 25 per cent. or over, the steel is quite appreciably attacked.

The data given in the preceding paragraphs concerning the austenitic steels relate to these materials after they have been heat treated in such a way as to produce a completely

* *Trans. A.S.S.T.* Sept., 1930, (Preprint).

austenitic structure. If, however, they contain free carbide in globular form, due to treatment at a temperature not quite high enough to produce a completely austenitic structure, their resistance to the boiling concentrated acid may be lowered to some extent if their chromium content is of the order of 16/18 per cent. but is not appreciably affected if this value is raised to 20 per cent. or more. Some typical values are given in Table LXXXII.

Free carbide due to a distinctly higher carbon content than usual in the steel exerts a similar effect and to an extent which obviously depends on the actual amounts of carbon and chromium in the steel.

TABLE LXXXII

Effect of Treatments producing Free Carbide in Austenitic Steels on Resistance to Boiling Nitric Acid.

Carbon %	Chromium %	Nickel %	Treatment Temperature.	Rate of attack : grs. per sq. m. per hour.	
				65% Acid (S.G. 1·42).	95% Acid (S.G. 1·50).
0·14	16·3	10·5	W.Q. 900° C. ...	2·01	1·48
			,, 1,100° C. ...	0·27	0·49
0·13	20·1	9·0	,, 900° C. ...	0·32	0·54
			,, 1,100° C. ...	0·48	0·20
0·15	24·2	11·2	,, 900° C. ...	0·17	0·28
			., 1,100° C. ...	0·15	0·40

The passivity effects produced by nitric acid on stainless steels—and particularly the austenitic chromium-nickel steels and the higher chromium stainless irons—should be carefully noted by those carrying out corrosion tests on samples submitted to them. Previous immersion in nitric acid, though producing no visible effect, may either prevent the attack of some other acid—inorganic or organic—on the sample or else retard its onset considerably. Sheets and plates used for the construction of chemical equipment are frequently pickled in baths containing this acid and hence their surfaces acquire an extra degree of passivity. Such extra protection is useful but it cannot always be relied on

in completed equipment as the protective skin, which presumably forms on the steel surface, may be damaged in fabrication processes. Hence it is generally preferable to regard this passivity effect of nitric acid as an extra protection which may be present but is not necessarily inherent in the material. For this reason it seems advisable to use, for laboratory tests, samples which have not been given this extra protection ; in the case of samples of unknown origin, this can only be assured by a careful re-preparation of their surfaces.

The property of all stainless steels, containing not less than about 10 per cent. chromium, of resisting almost completely the attack of nitric acid of specific gravity 1·20 at atmospheric temperature is particularly useful as it affords a certain means of identifying such steels should they be accidentally mixed up with ordinary steels. The latter are, of course, violently attacked by this acid.

In all that has been said in the preceding paragraphs relating to nitric acid, it has been assumed that the acid is reasonably pure. This occurs in all stages of the manufacture of the acid by methods based on the oxidation of synthetic ammonia or on other processes for the fixation of atmospheric nitrogen ; hence, the stainless irons and steels have been used with the greatest success for the construction of plant for carrying out such processes. On the other hand, Chile saltpetre, the other important raw material for the manufacture of the acid, contains notable amounts of chlorides and iodides as impurities. During the early stages of the manufacture of nitric acid from saltpetre, these impurities find their way into the acid and such impure acid has an appreciable attack on stainless steels. Hence these steels should only be employed for plant for handling the purified acid.

Sulphuric Acid. Solutions of this acid, especially if dilute, have always been regarded as among the most corrosive fluids to be handled in the chemical industry. As such solutions are very widely employed in many chemical processes, the production of metals possessing a notable degree of resistance to their action is of considerable importance.

The plain chromium steels are not generally useful where sulphuric acid is concerned. This may be illustrated by

the figures given in Table LXXXIII and obtained by Dr.
Hatfield* on a series of chromium steels.   The test samples
were immersed n 10 per cent. acid at atmospheric tempera-
ture for 24 hours.

TABLE LXXXIII

Action of Sulphuric Acid (10%) on Chromium Steels.

Carbon %	Chromium %	Loss in weight in 24 hours.
0·39	nil	0·1032 grams.
0·88	5·10	0·2198
0·64	8·96	0·3048
0·29	10·06	0·2143
0·56	12·47	0·2496
0·50	15·6	0·4279
0·49	19·66	0·3530
0·53	24·22	0·4543
0·58	32·07	0·5583

On the other hand, when nickel is added to steel, the
rate of solution of the latter in sulphuric acid is greatly
retarded ; see Table LXVII, page 300.   Nickel has a similar
protective effect on high chromium steels when added in
sufficient bulk to the latter to produce the austenitic type
of steel.   The rate of attack of various concentrations of the
acid, at atmospheric temperature, on austenitic steels con-
taining 15/20 per cent. chromium and 12/7 per cent. nickel
may be represented by a curve such as that marked A in
Fig. 186.   This actually refers to an alloy containing about
15 per cent. chromium and 10 per cent. nickel but results of
a similar order are obtainable from other compositions
within the range mentioned above.   For comparison, curve B
represents the rate of attack on a sample of mild steel under
the same conditions.   Curve A indicates that at atmospheric
temperatures, the chromium-nickel steel possesses a fair
degree of resistance against solutions containing up to about
15 or 20 per cent. of acid and also those containing more than
75 per cent.   The rate of attack, especially of the dilute acid,
rises rapidly, however, if the temperature be raised ; thus
curve C gives the results obtained at 40°C.

* *J.I.S.I.*, 1923, II, p. 103.

Pilling and Ackermann* came to the conclusion that the addition to chromium steels of nickel in amounts up to about 12/13 per cent. resulted generally in a progressive reduction in the rate of attack of dilute (5 per cent.) sulphuric acid, but that no further benefit accrued from a greater amount than this, even to the extent of replacing the iron entirely by nickel. Their results, however, were obtained at atmospheric temperature and a similar conclusion would certainly not be
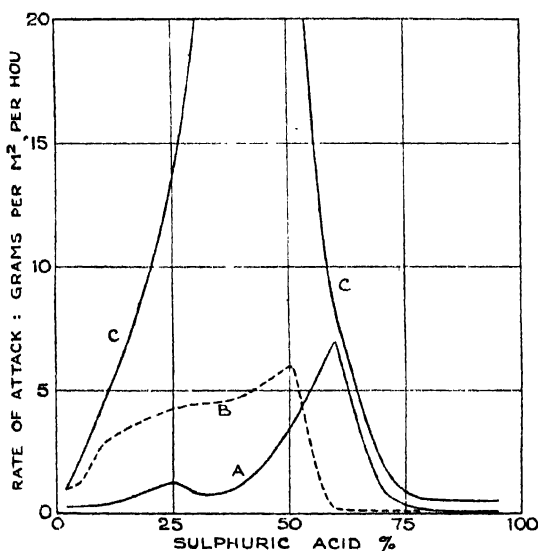
Fig. 186.   Rate of attack of sulphuric acid :—
Curve A.   On " Anka " steel at 15° C.
  „   B.   „   mild steel at 15° C.
  „   C.   „   " Anka " steel at 40° C.

warranted if acid at a higher temperature was in question. It should also be noted that the method of heat treatment which Pilling and Ackermann used (slowly cooling in a furnace from 1,000°C.) was such as to impair considerably the corrosion resistance of many of the austenitic steels they tested.

The beneficial effect of a relatively high nickel content is evident from results obtained by Dr. Hatfield† from whose work the data given in Table LXXXIV are taken.   In the

* *Loc. cit.*
† "Acid Resisting Steels." *Metallurgia*, Nov., 1929, p. 17.

tests recorded here, the samples (each weighing about 32 grams and having a surface area of about 15 sq. cm.) were immersed separately in 80 c.c. of acid for 24 hours.* The figures give the losses in weight per sq. cm., the word " max " indicating that attack was so rapid as to lead to the complete exhaustion of the acid within the period of the test.

* TABLE LXXXIV

Nickel Content and Rate of Attack of Sulphuric Acid.

Mark.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A	0·17	0·37	0·27	17·43	8·07
B	0·06	0·16	0·15	18·33	24·47

| Acid | Loss in weight (grams per sq. cm.). | | | | | |
| % | 20° C. | | 60° C. | | Boiling Point. | |
	A.	B.	A.	B.	A.	B.
0·25	0·0000	0·0001	0·0013	0·0012	Max.	0·0023
0·5	0·0004	0·0002	0·0029	0·0012	Max.	0·0013
1·0	0·0004	0·0003	0·0042	0·0020	0·0271	0·0017
2·5	0·0010	0·0003	0·0147	0·0034	0·0622	0·0021
5·0	0·0027	0·0003	0·0297	0·0039	0·1343	0·0043
10	0·0021	0·0003	0·0491	0·0054	0·2394	0·0047
20	0·0180	0·0007	0·1228	0·0074	0·5080	0·0920
35	0·0541	0·0012	0·1721	0·0224	0·6310	0·6472
50	0·0820	0·0015	0·4090	0·0250	0·4860	0·6645
65	0·0153	0·0038	0·1620	0·0215	1·1215	1·1695
80	0·0047	0·0007	0·0353	0·0209	0·7795	0·6190
95·6	0·0017	0·0014	0·0029	0·0013	—	—

The addition of 2 or 3 per cent. silicon to a steel similar to the one of higher nickel content used by Dr. Hatfield serves to increase its resistance to cold sulphuric acid, but again, the behaviour with hot acid is not good.   Table LXXXV gives data relative to such a steel and also, for comparision, to a

* The use of a small bulk of acid and a 24-hour duration of test leads, of course, to a distinct weakening of the acid strength in tests where the rate of attack is other than slight, and hence to low values if the losses in weight are returned in terms of time. Where the rates of attack in Table LXXXIV are low, and it is only under such conditions that the steels are of any commercial value, the figures given may be converted into " grams per sq. metre per hour " by multiplying by the factor 10,000/24.

high nickel alloy of the " nichrome " type ; the latter behaves far better with the hot acid.

TABLE LXXXV

Effect of Sulphuric Acid on Nickel-Chromium Alloys.

Mark.	Carbon %	Silicon %	Chromium %	Nickel %
A	0·34	2·35	17·7	25·8
B	0·41	0·50	11·1	64·3

Acid %		Rate of attack : grams per sq. m. per hour.			
		15° C.		60/65° C.	
By Volume.	By Weight.	A.	B.	A.	B.
5	8·5	0·15	0·12	—	—
35	47	0·12	0·11	—	—
50	62	0·20	0·08	—	—
10	16	- -	—	16·7	1·27
20	30	—	—	45·7	1·08
30	42	—	—	68·5	1·05

TABLE LXXXVI

Effect of Sulphuric Acid on Nickel-Chromium-Silicon Alloys (Dr. Mathews).

Mark.	Carbon %	Silicon %	Chromium %	Nickel %
A	0·25 max.	4·5/5·5	10/12	24/26
B	0·25 max.	4·5/5·5	10/12	33/35

Rate of attack : grams per sq. m. per hour.

Acid %	Temp.	Alloy A	Acid %	Temp.	Alloy A	Alloy B
1	20° C.	0·108	10	87°/90°	0·54	0·54
2	,,	0·101		boiling	1·55	0·77
8	.,	0·098	25	do.	1·86	0·59
4	,,	0·116	80	87°/90°	0·31	—
8	,,	0·108	92	39°	0·62	0·155
16	,,	0·054		69°	0·62	0·31
80	,,	0·071		—	—	—
50	,,	0·024		—	—	—

Dr. Mathews* reports that the addition of 4·5/5·5 per cent. silicon to alloys containing 10/12 per cent. chromium, together with either about 25 or 35 per cent. nickel produces materials very resistant to sulphuric acid. He quotes the data given in Table LXXXVI as evidence of this; the results with hot acid are particularly good.

The resistance of the austenitic chromium-nickel steels to dilute sulphuric acid may be increased very considerably by the addition to them of other metals, particularly molybdenum. Fig. 187, for example, summarises the results of experiments on a steel containing about 3½ per cent. of this
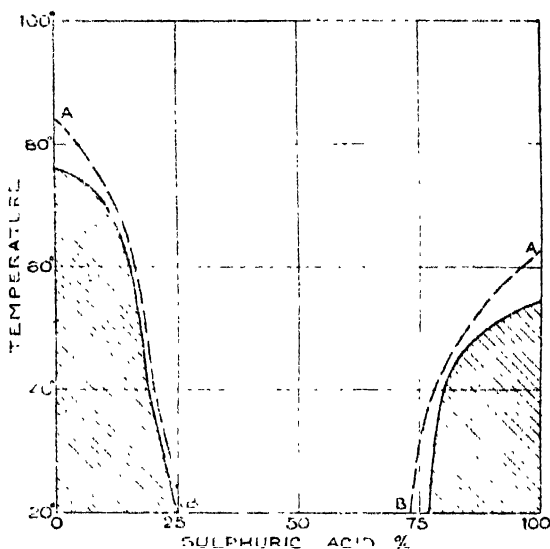
Fig. 187. Action of sulphuric acid on steel containing 0·13 per cent. carbon, 17·2 per cent. chromium, 10·1 per cent. nickel, 3·42 per cent. molybdenum. In the range of concentration and temperature included in the shaded areas, the rate of attack is nil or less than 0·1 gram per sq. m. per hour.

metal. The ordinates here are temperature and acid concentration and in the shaded areas the rate of attack was either nil or less than 0·1 gram per square metre per hour. In the narrow strips between the shaded areas and the broken lines AB, the rate of attack lay between 0·1 and 1·0 grams per square metre per hour. Beyond these lines, action proceeded at greatly increased rates, the molybdenum steel

* * "Recent Developments in Corrosion-Resistant and Heat-Resistant Steels." J. Ind. & Eng. Chem., December, 1929.

being attacked in many cases at distinctly faster rates than one free from molybdenum but otherwise similar in analysis ; see Table LXXXVII.

TABLE LXXXVII

Effect of Molybdenum on the Resistance of Chromium-Nickel Steels to Sulphuric Acid.

Mark.	Carbon %	Chromium %	Nickel %	Molyb-denum %
A	0·12	14·9	10·7	nil
B	0·13	17·2	10·7	3·42
C	0·34	20·1	8·6	nil
D	0·44	20·5	6·5	3·8

Rate of attack : grams per sq. m. per hour.

Acid % (by weight).	15° C.		40° C.		Acid % (by weight).	15° C.		60/65° C.	
	A.	B.	A.	B.		C.	D.	C.	D.
5	0·26	nil	2·02	nil	8·5	0·87	nil	—	—
10	0·37	nil	4·4	nil	16	0·98	nil	4·2	nil.
15	0·66	nil	6·73	nil	23·5	1·3	0·9	—	—
20	0·98	nil	10·0	2·6	30	1·3	1·4	119	158
25	1·23	nil	9·4	11·0	36·5	2·0	2·7	—	—
30	0·80	1·5	19·2	15·5	42	---	—	177	297
40	1·12	4·1	20·6	150	48	3·0	7·1	—	
50	3·35	6·0	100	150	62	3·9	6·1	—	
60	6·95	10·0	7·9	25	—	—	—	—	
70	0·91	1·2	1·97	12·5	---	—	—	—	
80	0·04	nil	0·54	nil	--	—	—	—	
90	—	nil	0·44	nil	—	—	—	—	
95	0·27	nil	0·50	nil	---	—	—	—	

The chromium-nickel-molybdenum steels are particularly valuable in their resistance to hot dilute solutions of sulphuric acid as such solutions are much used in chemical processes, for example, in the dyeing of textiles ; although they may be attacked by these acids when boiling, even when the concentration is as low as one per cent. or so, the rate of attack is distinctly less rapid than with most other varieties of chromium-nickel steels.

Tungsten also acts in somewhat the same fashion as

molybdenum but is not so effective. The addition of copper to the steels also retards greatly the rate of attack of sulphuric acid on them ; in this case, also, there is no medium range of concentration of acid producing a relatively rapid attack. Data relating to tungsten and copper steels are given in Table LXXXVIII and one may note the almost equal resistance possessed by the copper steel to all strengths of the acid.

TABLE LXXXVIII

Effect of Copper and Tungsten on the Resistance of Chromium-Nickel Steels to Sulphuric Acid.

Mark.	Carbon %	Chromium %	Nickel %	Copper %	Tungsten %
A	0·26	17·4	10·9	2·45	nil
B	0·29	17·7	9·73	nil	1·64

Acid % (by weight).	Rate of attack · grams per sq. m. per hour.			
	Steel A.		Steel B.	
	15° C.	40° C.	15° C.	40° C.
2	0·16	0·54	nil	nil
5	0·13	0·64	0·18	nil
10	0·18	0·77	0·67	9·5
15	0·16	0·66	1·08	6·5
20	0·16	0·42	1·49	14·6
25	0·24	0·74	2·08	—
30	0·29	1·16	2·75	—
40	0·31	0·72	4·78	— ·
50	0·18	1·03	8·81	····
60	0·29	1·56	9·26	—
70	0·13	2·10	0·79	14·7
80	0·26	0·21	nil	0·62
90	0·24	0·19	nil	0·51
95	0·13	0·13	nil	0·10

It has been found that the action of dilute sulphuric acid on stainless steels is much retarded, and may be altogether prevented, if the acid solution contains ferric sulphate or copper sulphate. In addition to being of distinct interest from a scientific point of view, the effect of these salts on the action of sulphuric acid has considerable practical

importance.   Many mine waters, which are notoriously
corrosive in their action on pumping machinery owing to the
presence of free sulphuric acid, contain, also appreciable
quantities of either or both of these salts, and as a result
they have often no effect on stainless steels, even the 12/14
per cent. chromium variety, though they attack ordinary
steel and other metals quite rapidly.   It is not out of place
therefore, to devote some attention to the action of these
salts.
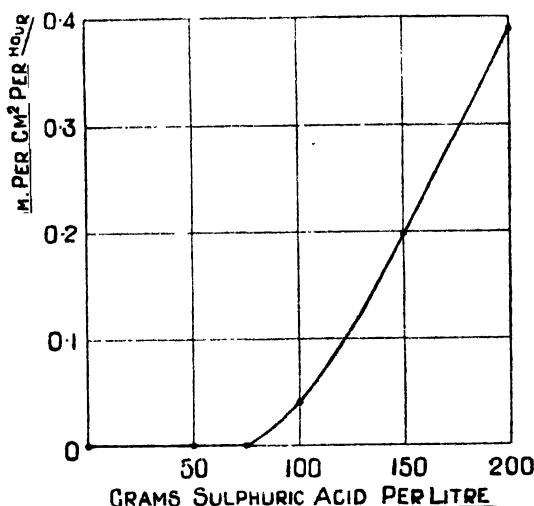
Fig. 188.   Rate of attack (on 12·6 per cent. chromium steel) of solutions of
copper sulphate, 100 grams per litre, containing also the amounts of free sulphuric
acid indicated.
N.B.— 0·1 mgm. per cm² per hour = 1·0 gram per sq. m. per hour.

The effect, on stainless material, of solutions containing
both copper sulphate and sulphuric acid depends on the
actual and the relative amounts of these two substances
present in solution and on the composition of the steel.   It
may be illustrated by considering a 12/14 per cent. chromium
steel.   A solution of copper sulphate itself, as mentioned
earlier, has no action on this steel : on gradually adding
sulphuric acid to the copper sulphate solution, no action
takes place until a certain amount of acid is present, depend-
ing on the actual concentration of the copper sulphate
in solution.   After this critical amount is exceeded, the action
of the acid liquor becomes more and more intense as the
concentration of acid increases.   This is illustrated by the

curve in Fig. 188, which gives the results of the action for
24 hours at atmospheric temperature of solutions, each
containing 100 grams of copper sulphate* per litre but with
different amounts of sulphuric acid, on a number of
hardened and tempered samples of stainless steel containing
0·80 per cent. carbon and 12·6 per cent. chromium.
Attack was produced when the concentration of the free acid
reached 100 grams per litre.

On the other hand, if small but gradually increasing
amounts of copper sulphate be added to sulphuric acid, the
rate of attack on the steel at first increases rapidly.
In such cases, copper is deposited as a flocculent mass on the
steel and no doubt sets up electrochemical action.   As the
concentration of the copper increases, however, the attack
suddenly falls off very rapidly and finally ceases altogether.
This effect is as shown in curves A and B in Fig. 189.   The
former refers to the attack of liquor containing 100 grams
sulphuric acid per litre and the latter to solutions containing
50 grams of the acid per litre.   The duration of attack in
all cases was 24 hours at atmospheric temperature and the
steel was similar to that used for the last experiment.
The curves show that the amount of copper sulphate required
to prevent action varies with the acid strength and is relatively
less as the concentration of acid is lowered.

The resistance of the 12/14 per cent. chromium steel to
the attack of sulphuric acid when sufficient copper sulphate
is present would appear to be due to a species of passivity
somewhat similar to that produced in ordinary steel by
strong nitric acid and other reagents, as mentioned on page
258.   There are also other points of resemblance, thus the
passivity produced in stainless steel by the action of copper
sulphate persists for some time after the sample is removed
from the solution producing passivity.   This is notably the
case if the samples are transferred to solutions in which the
concentration of copper sulphate is gradually reduced.   For
example, a sample of stainless steel was placed in a solution
containing 50 grams each of sulphuric acid and copper
sulphate per litre ; such a solution, as shown in Fig. 189, has
no action on the steel.   At intervals of one or two days, the
sample was transferred to solutions containing the same

* In all the results with this salt, the weights given refer to the crystalline
material ($CuSO_4. 5H_2O$).

amount of free acid but with gradually decreasing amounts of copper sulphate. The concentration of the latter was reduced to 2·5 grams per litre without any action taking place, although
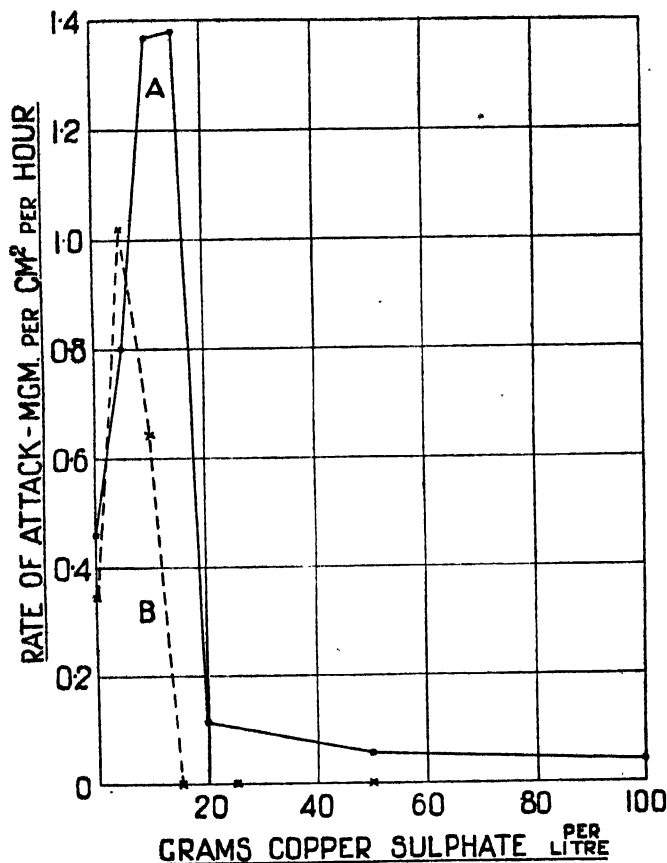
FIG. 189. Effect of copper sulphate on the rate of attack of dilute sulphuric acid on stainless steel at 15°/20° C.

Curve A. 100 grams free sulphuric acid per litre.
,, B. 50 ,, ,, ,, ,, ,, ,,

(N.B.—0·1 mgm. per cm² per hour = 1·0 gram per sq. m. per hour.)

under normal conditions the steel was attacked by similar acid liquor containing 10·0 grams or less of copper sulphate per litre. On reducing the strength to 2·0 grams per litre, the steel was very slowly attacked, producing a gradual darkening of the steel surface. The sample was allowed

to remain in this acid liquor for 7 weeks ; at the end of this period it had a polished black surface, with a greenish tint, very similar to that of the "oxidised" finish of ordinary steel. The total loss in weight of the sample in the 7 weeks' attack was only 0·014 per cent. of its original weight, equivalent to a rate of attack of 0·0024 grams per square metre per hour.

In the same way the concentration of copper sulphate in acid liquor containing 100 grams sulphuric acid per litre in which a similar piece of stainless steel was placed was gradually reduced from 250 grams to 7·5 grams per litre without any action taking place. When reduced to 5 grams per litre, however, a similar slow action to that described above took place ; the sample gradually acquired a polished black surface and after 7 weeks' attack had lost 0·019 per cent. of its original weight, equivalent to a rate of attack of 0·003 grams per square metre per hour.

The extent of the passivity produced in these two cases will be more easily realised when it is remembered that under normal conditions, the samples would have lost well over 50 per cent. of their weight during a 7 weeks' immersion in such acid liquors.

The passivity produced by acid copper sulphate solutions of suitable strength also persists for some considerable time if the samples are taken out of the solution producing passivity, dried and then left in this condition. For example, the sample used for the test in liquor containing 50 grams of sulphuric acid and 25 grams of copper sulphate per litre (Fig. 189 curve B) was cleaned and dried after the 24 hours' immersion, which produced no attack, and put away in a box for 2 months. It was then placed in liquor containing 100 grams of acid and 10 grams of copper sulphate, i.e., liquor which, as shown in curve A, Fig. 189, attacks the normal material rapidly. No action was visible for 3 or 4 days, after that the sample gradually darkened in colour. At the end of 34 days, it was taken out and had a shiny greenish black surface similar to the two samples described above. The total loss in weight produced in the 34 days' attack was 0·009 per cent. of the original weight, equivalent to 0·0019 grams per square metre per hour.

•   Again the passivity effect is rendered more striking by noting that a similar sample which had not previously

been made passive lost practically 1·9 per cent. of its weight in 24 hours when immersed in acid liquor of this same strength and would therefore have lost considerably more than half its weight in 34 days.

The effect of copper sulphate in thus producing passivity is more pronounced the higher the chromium content of the steel. It is extremely effective in the case of the austenitic chromium-nickel steels; very small quantities suffice to prevent the attack on such steels of dilute sulphuric acid even when hot, as may be seen from the results quoted in Table LXXXIX.

TABLE LXXXIX

Action of Copper Sulphate on the attack of Sulphuric Acid on " Anka " Steel.

Carbon	Chromium	Nickel
0·12	14·9	10·7

Strength of Solution (grams per litre).		Rate of attack : grams per sq. m. per hour.				
Sulphuric Acid.	Copper Sulphate.	20° C.	40° C.	60° C.	80° C.	Boiling.
100	nil	0·95	1·80	9·7	45·6	83·2
,,	0·05	2·07	3·11	13·4	—	—
,,	0·10	nil	nil	15·1	—	—
,,	0·15	—	—	11·5	85·0	—
,,	0·20	nil	nil	nil	49·1	—
,,	0·25	nil	nil	nil	nil	245
,,	0·3	—	—	—	—	232
,,	0·4	—	—	—	—	250
,,	0·5	nil	nil	nil ·	nil	nil

The action of ferric sulphate in retarding or preventing the attack of sulphuric acid on stainless steel was first pointed out by Dr. Hatfield* who also showed that the amount of ferric sulphate required to prevent action varied with the condition of the steel, whether hardened or hardened and tempered, and also, with any one material, was proportional to the amount of free sulphuric acid present.

* "The Development of Stainless Steel." Messrs. T. Firth & Sons.

Experiments carried out by the author on hardened and tempered material containing 0·8 per cent. carbon and 12·6 per cent. chromium are given in Table XC. The actual concentration of ferric sulphate producing passivity is probably affected to some extent by slight variations in temperature, or other conditions. Thus a duplicate sample in liquor containing 15 grams ferric sulphate per litre, tested a few days after the one described in Table XC, remained quite unattacked after being immersed for a month in the liquor.

TABLE XC

Action of Ferric Sulphate on the attack of Sulphuric Acid on Stainless Steel at 15°/20°C.

Strength of Solution (grams per litre).		Duration of Test.	Loss in gr ms per sq. m. per hour.
Sulphuric Acid.	Ferric Sulphate.		
100	nil	24 hours	5·6
,,	5	,,	6·2
,,	10	,,	6·6
,,	15	,,	7·3
,,	20	36 days	Not attacked
,,	40	,,	,,
,,	60	,,	,,

It will be seen that there is a slight increase in the rate of attack when only small amounts of ferric sulphate are present, though the increase is not nearly so great as with copper sulphate and understandably so. As with the latter salt also, the passivity produced by ferric sulphate persists for some time after removing from the solution producing passivity, but apparently to a less degree than with the copper salt. For example, a sample of material similar to that used for the tests above was placed for 24 hours in liquor containing 100 grams each ferric sulphate and sulphuric acid, there being, of course, no attack. It was then transferred at intervals of 24 hours to solutions containing the same amount of acid, but with the ferric sulphate reduced successively to 50, 25, 15, 10, 5 and 2.5 grams per litre ; in each case there was no attack. The sample was then transferred to a similar solution but containing only 2·0 grs. ferric sulphate per litre

and was vigorously attacked in a few minutes, the rate of attack being similar to that of such liquor on the normal steel.

It should be noted that ferrous sulphate has not the same effect as ferric sulphate ; a sample of 12 per cent. chromium steel placed for 24 hours in a solution containing 100 grams sulphuric acid per litre together with 200 grams ferrous sulphate per litre was attacked at practically the same rate as a similar sample placed in acid of the same strength but containing no ferrous sulphate, the rates of attack being 3·9 and 4·6 grams per square metre per hour respectively.

The practical importance of these interesting passivity effects lies, as mentioned earlier, in their application with regard to the pumping and handling of acid mine waters and other water containing free sulphuric acid.   Provided a sufficient amount of either ferric sulphate or copper sulphate or both is present in the water along with the free acid (and often mine waters contain these salts in relatively large quantities) such water will have no action on stainless steel though it will attack ordinary steel quite rapidly.   For example, mine waters having the following analyses, expressed in parts per 100,000 :

			A	B	C
Copper	...	...	16	14·7	4,400
Ferric Iron		...	188	71·2	300
Ferrous Iron		...	160	not given.	225
Free Sulphuric Acid			30	14·0	2,500

had no action on 12/14 per cent. chromium steel, though they attacked ordinary mild steel quite rapidly.

In addition, the examples given on pp. 368 and 367 of the persistence of passivity when the amount of copper or ferric sulphate was reduced considerably below the normally safe limit are also of considerable importance as they show that if, in the handling of such acid waters, the ratio of salt, producing the passivity, to acid is temporarily reduced to a figure normally unsafe, such reduction will not necessarily lead to any attack on the steel.

Mixtures of Sulphuric and Nitric Acids.   The addition of relatively small amounts of nitric acid to sulphuric acid of greater strength than about 30 per cent. retards and may prevent the attack of the latter on the austenitic chromium-nickel steels.   Below about 30 per cent. sulphuric

acid, the nitric acid addition may accelerate or retard the rate of attack, depending on circumstances. The results of tests on a steel of this type are set out in Table XCI.

TABLE XCI

Effect of small additions of Nitric Acid on the rate of attack of Sulphuric Acid on " Anka " Steel.

Carbon %	Chromium %	Nickel
0·12	14·9	10·7

(Rates of attack in grams per sq. m. per hour.)

Sulphuric Acid (by weight).	Temperature of Test and per cent. Nitric Acid present.									
	15° C.			40° C.			80/85° C.		110° C.	
	Nil	1%	3%	Nil	1%	3%	1%	3%	1%	3%
2	0·26	1·19	0·91	0·98	2·44	0·94	—	—	—	—
5	0·26	1·55	1·37	2·02	2·70	1·51	—	—	—	—
10	0·37	2·55	1·20	4·4	4·47	0·91	—	—	—	—
20	0·98	3·18	0·64	10·0	4·92	1·22	—	—	—	—
25	1·23	2·73	0·12	9·4	3·47	nil	2·35	0·4	9·15	2·53
30	0·80	2·06	0·04	19·2	1·65	0·31	—	—	—	—
40	1·12	0·08	0·08	20·6	0·22	0·05	—	—	—	—
50	3·35	nil	nil	100	nil	nil	1·05	0·45	5·3	5·5
75	0·5	nil	nil	1·0	nil	nil	0·35	0·28	9·7	5·34
85	0·1	nil	nil	0·5	nil	nil	0·36	0·49	3·63	3·14

The effect of these small nitric acid additions may perhaps be more easily visualised by the aid of Figs. 190 and 191. The former shows the accelerated attack produced when the nitric acid is added to dilute solutions of sulphuric acid. The latter figure indicates approximately, in a temperature-concentration diagram, the greatly increased resistance of the steel to stronger solutions of sulphuric acid due to similar additions. Within the range of concentration and temperature covered by the shaded area, the steel is attacked by the pure acid at a rate not exceeding 0·1 gram per square metre per hour. By the addition of 1 or 8 per cent. nitric acid, the limits of concentration and tempera-ture within which the steel possesses an equal resistance are

AA

extended to the lines ABC and DEF respectively. If the permissible rate of attack be increased to 1·0 grams per square metre per hour, the limits of useful service of the steel
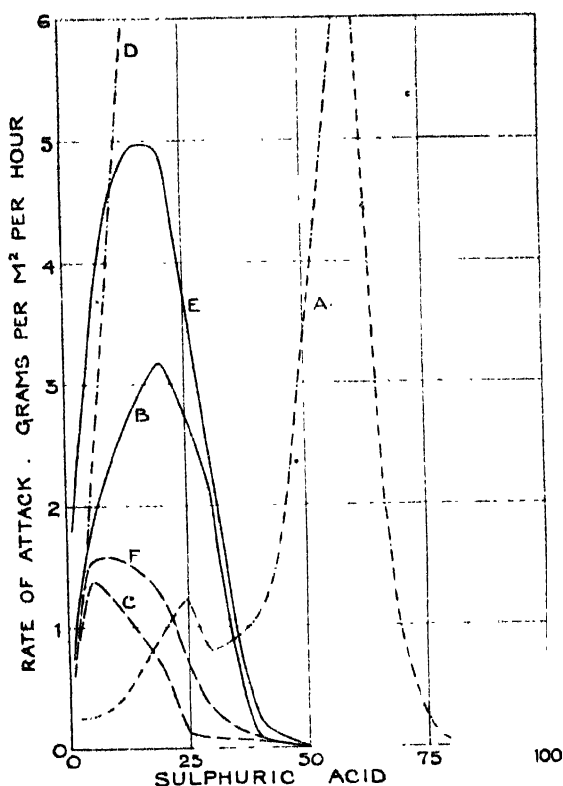
Fig. 190. Effect of small additions of nitric acid on the rate of attack of sulphuric acid on " Anka " steel ; 0·12 per cent carbon, 14·9 per cent. chromium, 10·7 per cent. nickel.

Curve	Nitric Acid %	Temperature %
A	nil	15° C.
B	1	15° C.
C	3	15° C.
D	nil	40° C.
E	1	10° C.
F	3	40° C.

with the 8 per cent. nitric acid mixture may be extended to the line XYZ.

The mixtures of sulphuric and nitric acids commonly used for nitrating purposes (which contain a greater proportion of the latter acid than was considered in the last few
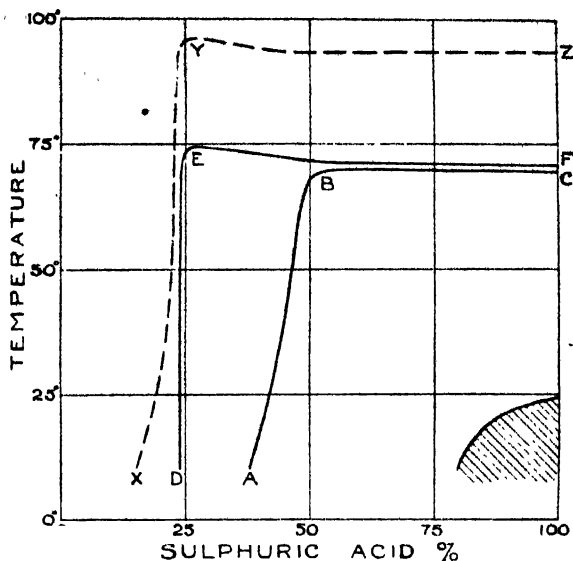
FIG. 191.   Effect of small additions of nitric acid on the rate of attack of sulphuric acid on " Anka " steel ; see page 369.

paragraphs) have practically no action on either the chromium or the chromium-nickel steels.   The results given in Table XCII and relating to tests in which the samples were immersed

TABLE XCII

Action of Nitrating Acids on Stainless Steels.

Composition of Steel.				Rate of attack: grams per sq. m. per hour.	
Carbon %	Chromium %	Nickel %	Silicon %	" Mixed " Acid. 69·0% H_2SO_4 20·5% HNO_3 10·5% H_2O	" Waste " Acid. 63·0% H_2SO_4 17·0% HNO_3 20·0% H_2O
0·19	12·0	0·21	0·22	0·0061	0·0054
0·08	15·4	0·30	0·26	0·0049	0·0058
0·21	20·6	2·61	0·28	0·0024	0·0019
0·10	15·2	11·4	0·25	0·0021	0·0014
0·10	17·2	7·9	0·30	0·0017	0·0010
0·34	17·7	25·8	2·35	0·0021	0·0013

in the respective mixtures for 6 months, are of interest in this connection.

Results of the same order are reported by Dr. Hatfield[*] in tests on a steel containing approximately 18 per cent. chromium and 8 per cent. nickel. These tests lasted two months, the temperature being 15°C. At 110°C., the rate of attack was higher but the results were still satisfactory, see Table XCIII.

TABLE XCIII

Tests with Nitrating Acids on " Staybrite."

Composition of Acid.			Temperature	Rate of attack:
$H_2SO_4\%$	$HNO_3\%$	$H_2O\%$	of Test.	grs. per sq. m. per hour.
29	69	2	15° C.	0·0007
54	44	2	,,	0·002
77	21	2	,,	0·002
90	8	2	,,	0·003
29	49	22	,,	0·0007
54	31	15	,,	0·0007
76	15	9	,,	0·0015
88	5·5	6·5	,,	0·0015
57	14	29	110° C.	0·17
57	10·5	32·5	,,	0·29
57	7	36	,,	0·17
57	3·5	39·5	,,	0·29

TABLE XCIV

Tests with " Mixed Acids " on " V.2.A."

Analysis of Acid.			Temperature	Rate of attack :
$H_2SO_4\%$	$HNO_3\%$	$H_2O\%$	of Test.	grs. per sq. m. per hour.
80	5	65	95° C.	0·1/1·0
30	10	60	boiling	0·1/1·0
20	15	65	50° C.	less than 0·1
			80° C.	,,
58	40	2	20° C.	,,
			60° C.	,,
			100° C.	0·1/1·0
			110° C.	3·0/10·0

Data obtained by Messrs. F. Krupp, A.G., may also be quoted ; these relate to their " V.2.A." steel, containing about 20 per cent. chromium and 7 per cent. nickel, and are given in Table XCIV.

Sulphurous Acid. The action of solutions of this acid depends very much on conditions. If perfectly pure—in particular, free from sulphuric acid—they have generally little or no action on the austenitic steels. If, however, oxidation takes place even in slight degree with the production of sulphuric acid, and this is not easy to avoid, some action is likely to be produced, the amount depending on temperature and degree of oxidation. These steels are also attacked by the pure acid at fairly high temperatures and pressures.

A considerably greater degree of resistance, both to the pure acid at high temperatures and pressures and also to the slightly oxidised acid, is obtained by the addition of molybdenum to the chromium-nickel steel. The improvement effected in connection with the oxidised acid will be understandable from the remarks already made regarding the resistance of molybdenum-containing steels to the action of sulphuric acid. As regards the effects of temperature and pressure, the data given in Table XCV and obtained by Messrs. F. Krupp, A.G.,* are of interest.

TABLE XCV

Action of Sulphurous Acid on Chromium-nickel (V.2.A.) and Chromium-nickel-molybdenum (V.4.A.) Steels.

(Solution saturated at atmospheric temperature.)

Pressure.	Temperature.	Rate of attack : grams per sq. m. per hour.	
		V.2.A.	V.4.A.
—	20° C.	less than 0·1	less than 0·1
4 atmospheres	135° C.	—	,,
5 to 8 ,,	160° C.	1·0/3·0	,,
10 ,,	180° C.	,,	,,
15 ,,	200° C.	,,	0·1/1·0
20 ,,	200° C.	,,	,,

* "Nichtrostender Stahl." Messrs. F. Krupp, A.G.

The advantages of the chromium-nickel-molybdenum steels for use in connection with sulphurous acid at high temperatures and pressures were claimed by Messrs. F. Krupp, A.G., in their original patent* covering the use of these steels.

The data given above refer to aqueous solutions of sulphur dioxide at temperatures up to their boiling points under high or low pressures as the case may be. The action of sulphur dioxide gas, unaccompanied by liquid moisture (e.g., in flue gases resulting from the combustion of more or less sulphurous fuels) falls in a rather different category ; it will be considered in the next chapter.

Hydrochloric Acid. This acid attacks all forms of stainless steel, the plain chromium steels having little or no greater resistance than ordinary mild steel. The rate of attack of cold dilute solutions of the acid on the austenitic chromium-nickel steels is very slow, however, and it is further reduced by the addition of molybdenum or copper. When heated, however, even the very dilute solutions may have a comparatively rapid attack on all these alloys, the best results being probably given by molybdenum-containing steels. The limited use which may be obtained from the steels,

TABLE XCVI

Action of Hydrochloric Acid on Austenitic Steels.

(Rates of attack in grams per sq. m. per hour.)

Composition of Steel					Temperature of Test.	Concentration of Acid (by weight).					
Carbon %	Chromium %	Nickel %	Copper %	Molybdenum %		0·5%	1%	2%	5%	10%	25%
0·10	15·2	11·4	—	---	15° C.	0·10	0·12	0·43	1·35	1·71	19·9
					40° C.	2·13	2·21	4·0	5·0	16·1	—
					60° C.	9·4	8·4	24·9	—	—	—
					80° C.	29·4	—	—	—	—	—
					b.p.	55·6	—	—	—	—	—
0·10	17·8	10·1	2·2	—	15° C.	nil	0·04	0·11	0·13	0·21	3·1
					40° C.	0·27	0·60	0·30	0·64	1·52	—
					60° C.	0·90	0·81	2·02	4·03	8·98	—
					80° C.	5·0	—	—	—	—	—
					b.p.	13·0	—	—	—	—	—
0·13	17·2	10·1	—	3·42	15° C.	nil	nil	nil	0·96	2·5	12·5
					40° C.	nil	nil	nil	5·67	36·0	—
					60° C.	nil	nil	13·7	—	—	—
					80° C.	nil	nil	—	—	—	—
					b.p.	25·5	113	—	—	—	—

* British patent 201,915 (July, 1923); German patent 399,808 (August, 1922).

simple or complex, is illustrated in the data given in Table XCVI.

Boric Acid A solution of this acid, saturated at atmospheric temperature, has no action on stainless steels (including the 12/14 per cent. chromium variety) even at its boiling point. A solution saturated at its boiling point has,

TABLE XCVII

Action of Boric Acid on Stainless Steel

Carbon %	Chromium %	Nickel %	Temperature of Test	Rate of attack (grams per sq m per hour) of solutions saturated at	
				15° C	B p.
0·09	13·5	0·30	15° C.	nil	
			boiling	nil	0·57
0·09	16·1	0·17	15° C.	nil	
			boiling	nil	0·35
0·12	14·9	10·7	15° C.	nil	
			boiling	nil	nil

TABLE XCVIII

Action of Chromic Acid on Stainless Steels.

(Rates of attack in grams per sq. m. per hour.)

Composition of Steel.					Temperature of Test	Concentration of Acid	
Carbon %	Chromium %	Nickel %	Copper %	Molybdenum %		10%	Saturated at 15° C.
0·09	13·5	0·30	—	—	15° C.	nil	0·89
					40° C.	nil	1·4
					b.p.	0·31	45·1
0·12	14·9	10·7	—	—	15° C.	nil	0·63
					40° C.	nil	1·17
					b.p.	0·52	31·6
0·10	17·8	10·1	2·20	—	15° C.	—	1·47
					40° C.	—	7·36
					b.p.	0·64	73·5
0·13	17·2	10·1	—	3·12	15° C.	—	3·15
					40° C.	—	10·0
					b.p.	0·59	108

however, a slight action on the plain chromium steels, the rate of attack diminishing somewhat with increasing chromium content, but has still no action on the austenitic chromium-nickel steels ; see Table XCVII.

Chromic Acid. The action of commercial samples of this acid is likely to vary considerably with their freedom or otherwise from sulphuric acid. The results given in Table XCVIII were obtained from the ordinary "chemically pure" reagent. It will be noted that the 12/14 per cent. chromium iron possesses as good a resistance as the austenitic alloys and that the rate of attack on the latter is increased by the addition of copper or molybdenum to them.

Phosphoric Acid. An accurate evaluation of the action of this acid on various types of stainless steel is somewhat difficult to obtain owing to the ease with which the metal assumes a passive condition when immersed in solutions of the acid, even of those which may attack it very rapidly should this passive condition be temporarily broken down. And unfortunately, the conditions which may induce passivity or lead to its breakdown are very obscure   For this reason the results obtained on single tests on a given sample of steel may quite easily lead to very erroneous conclusions being drawn as to its value for use with the acid   In the results given in Table XCIX, the author has represented the several steels in their worst light ; these results are based on numerous tests and occasional good results in the series have been ignored if duplicate test pieces were attacked.

It will be seen that none of these materials is of any value for use with the concentrated acid at temperatures approaching 110°C. A high chromium content is undoubtedly helpful in giving greater resistance to more dilute solutions of the acid or to the concentrated form at lower temperatures ; but austenitic chromium-nickel steels with as high a content of the former metal as 24·3 per cent. were still violently attacked by the concentrated acids at 110°/115°C   Probably the best result under such corrosive conditions is obtained by using a chromium-nickel-molybdenum steel. The rates of attack on such a steel (containing 17·2 per cent. chromium ; 10·1 per cent. nickel ; 3·42 per cent. molybdenum) by acids of specific gravity 1·50 and 1·75, at 110°/115°C., were 2·16 and 1·12 grams per square metre per hour respectively.

TABLE XCIX

Action of Phosphoric Acid.

(Rates of attack in grams per sq. m. per hour.)

Carbon %	Chromium %	Nickel %	Temperature of Test.	Concentration of Acid.			
				5%	25%	66 3% (S.G. 1·5)	90% (S.G. 1·75)
0·10	15·5	0·39	15°C.	0·7	18·5	47·2	nil
			80° C.	1·61	—	—	0·15
			boiling	—	—	—	800
0·10	17·9	0·38	15° C.	nil	17·4	50·9	nil
			80° C.	nil	—	—	nil
			boiling	nil	—	—	1600
0·12	14·9	10·7	15° C.	nil	0·08	0·15	nil
			80° C.	nil	nil	35·9	2·2
			110° C.	—	—	112	16·7
			boiling	nil	0·05	—	1170
0·14	16·3	10·5	15° C.	nil	nil	nil	nil
			60° C.	nil	nil	nil	nil
			80° C.	nil	nil	32·4	nil
			boiling	nil	nil	53·4	2110
0·12	18·0	8·2	15° C.	nil	nil	nil	nil
			80° C.	nil	nil	nil	0·92
			110° C.	—	—	72·9	9·0
			boiling	nil	nil	—	1520
0·18	20·1	9·0	15° C.	nil	nil	nil	nil
			80° C.	nil	nil	nil	nil
			boiling	nil	nil	72·7	1280

TABLE C

Action of Phosphoric Acid on Austenitic Steels.

Acid %	Specific Gravity.	Temperature of Test.	Rate of attack (grams per sq. m. per hour).		
			V.2.A. Chromium-Nickel.	V.4.A. Chromium-Nickel-Molybdenum.	V.6.A. Chromium-Nickel-Copper.
1	1·0054	20° C.	less than 0·1	less than 0·1	less than 0·1
1	1·0054	boiling	,,	,,	,,
1	1·0054	140° C. at 3 atmos. press.	,,	,,	,,
10	1·0567	boiling	,,	,,	,,
45	1·3059	,,	,,	,,	,,
80	1·645	110° C.	over 10·0	1·0/3·0	over 10·0
80	1·645	115° C.	..	..	..

The data given in Table C are taken from publications of Messrs. F. Krupp, A.G.; they agree with those in the preceding table.

Acetic Acid is often regarded as an organic acid of only moderate strength; it is, however, an extremely corrosive acid and there are few metals which will completely resist its action under any and every condition of concentration and temperature.

The plain chromium steels are undoubtedly more resistant to acetic acid than ordinary steels, the complete stability of an ordinary stainless steel knife against vinegar being a familiar example. As already pointed out, however, part of the immunity in this case (and in others, e.g., fruit juices, involving dilute solutions of organic acids) is due to organic matter present in colloidal form; actually a pure solution of acetic acid of the same strength as vinegar (4 or 5 per cent.) slowly attacks a 12/14 per cent. chromium steel

TABLE CI

Action of Acetic Acid on Stainless Iron.

Carbon %	Chromium	Nickel %
0·08	15·4	0·20

(Rates of attack in grams per sq. m. per hour.)

Temp- erature.	Concentration of Acid.					
	5%	15%	33%	60%	80%	100%
15° C.	nil	0·09	0·26	1·13	0·42	nil
40° C.	1·0	3·75	5·1	3·1	1·07	0·1
80° C.	3·26	6·53	—	—	—	1·62

even at atmospheric temperature. Table CI gives data relative to a stainless iron containing about 15 per cent. chromium and, as will be seen, the range of usefulness of such material is limited. A greater degree of resistance at atmospheric temperature may be obtained by increasing the chromium content, but even with as high a value as 22/23

per cent. rapid attack occurs with hot acid of medium con-
centration.

Much better results are obtainable from the austenitic
chromium-nickel steels, but as shown in Table CII, attack

TABLE CII

Action of Acetic Acid on Austenitic Steels.

Mark.	Carbon %	Chromium %	Nickel %
A	0·10	15·2	11·4
B	0·15	17·5	7·9
C	0·18	20·2	8·8

(Rates of attack in grams per sq. m. per hour.)

M rk.	Temperature.	Concentration of Acid.						
		5%	10%	15%	33%	60%	80%	100%
A ...	15° C. 40° C. 80° C.	nil	nil	nil	nil	nil	nil	nil
	boiling ...	nil	2·94	3·5	7·9	7·6	5·4	2·2
B ...	15° C. 40° C. 80° C.	nil	nil	nil	nil	nil	nil	nil
	boiling ...	nil	3·12	4·3	7·22	8·1	7·3	2·0
C ...	15° C. 40° C. 80° C.	nil	nil	nil	nil	nil	nil	nil
	boiling ...	nil	nil	nil	2·93	14·3	6·85	1·5

still takes place with boiling acid except when the latter is
very dilute.   Here again a chromium content of about 20 per
cent. is an advantage in giving a greater range of complete
resistance, but it should be noted that when attack does
occur, it may take place at a greater rate with the higher
chromium steel.

Complete immunity from attack is not obtained by
using a still higher chromium content together with much

more nickel and a small amount of silicon ; see the results on steel A in Table CIII. The further data in this table show that the addition of molybdenum or copper to the chromium-nickel steels has a distinct beneficial influence. None of the alloys listed in this table was attacked at 80°/90°C. by acid of any concentration.

TABLE CIII.

Action of Boiling Acetic Acid on Complex Austenitic Steels.

Mark.	Carbon %	Chromium %	Nickel %	Silicon %	Copper %	Molybdenum %
A.	0·10	25·1	20·9	0·91	—	—
B.	0·10	17·8	10·1	0·36	2·2	—
C.	0·13	17·4	10·1	0·54	—	3·42
D.	0·35	20·9	10·6	0·54	—	3·78

(Rates of attack in grams per sq. m. per hour.)

Mark.	Concentration of Acid.						
	5%	10%	15%	33%	60%	80%	100%
A.	nil	nil	2·86	3·74	2·64	0·81	0·40
B.	nil	nil	1·5	2·25	4·96	0·75	0·45
C.	nil	nil	nil	nil	1·26	0·93	0·30
D.	nil	nil	nil	nil	nil	nil	nil

TABLE CIV.

Action of Acetic Anhydride on Stainless Steels.

(Rates of attack in grams per sq. m. per hour.)

Composition of Steel.					Temperature of Test		
Carbon %	Chromium %	Nickel %	Copper %	Molybdenum %	15° C.	80° C.	Boiling.
0·08	15·4	0·80	—	—	nil	nil	0·89
0·14	22·8	0·08	—	—	nil	nil	0·78
0·07	17·2	0·24	—	—	nil	nil	0·56
0·12	14·9	10·7	—	—	nil	nil⁻	0·56
0·12	14·9	10·7	—	—	nil	nil	nil
0·18	17·2	10·1	—	3·24	nil	nil	nil
0·26	17·4	10·9	2·45	—	nil	nil	nil,

It will be noticed from Tables CI to CIII that the rate of attack of the 100 per cent. acid is considerably less than that of 60/80 per cent. strength. The corrosive effect of acetic anhydride is still less marked ; the austenitic steels resist this compound completely, even when boiling, while the stainless irons possess a useful degree of resistance ; see Table CIV.

TABLE CV.

Action of Acetylating Mixtures on Stainless Steels.

(Rates of attack in grams per sq. m. per hour.)

Analysis of Steels.					
No.	Carbon %	Chromium %	Nickel %	Copper %	Molybdenum %
(1)	0·07	17·2	0·24	—	—
(2)	0·12	14·9	10·7	- ·	- -
(3)	0·18	20·2	8·8	- ·	— -
(4)	0·10	17·8	10·1	2·2	... -
(5)	0·13	17·4	10·1	—	3·42

No.	47½% Acetic Acid. 47½% Acetic Anhydride. 5 % Sulphuric Acid.			90% Acetic Acid. 10% Sulphuric Acid.	90% Acetic Acid 5% Sulphuric Acid. 5% Water.	33½% Acetic Acid. 33½ Acetic Anhydride. 33½ Zinc Chloride.	
	15° C.	40° C.	80° C	15° C.	15° C.	15° C.	40° C.
(1)	2·76	3·36	· ·	—	—	0·02	1·20
(2)	nil	nil	3·4	0·11	0·41	0·01	0·08
(3)	nil	nil	3·7	—	—	0·015	0·10
(4)	nil	nil	1·2	0·10	0·19	0·01	0·06
(5)	nil	nil	0·74	nil	nil	0·01	0·08

In the rayon industry, mixtures of acetic acid and acetic anhydride, together with some catalyst capable of absorbing water, such as sulphuric acid or zinc chloride, are used in the preparation of cellulose acetate ; these mixtures vary rather widely in composition and may be used at temperatures which are stated to lie between 25°C. and 70°C. Satisfactory resistance against quite a number of these solutions may be obtained with the austenitic chromium-nickel steels and still better results with those containing molybdenum in addition. The stainless irons are not so

good, though possibly in some cases they might be useful. The results of tests with a number of these solutions are* given in Table CV.

Carbolic Acid (Phenol). A 5 per cent. aqueous solution of this acid had no action, either at atmospheric temperature or at boiling point on stainless iron or steel (12/14 per cent. chromium) or on an austenitic steel containing 14·9 per cent. chromium and 10·7 per cent. nickel.

Citric Acid. Even dilute solutions of this acid attack the ordinary 12/14 per cent. chromium steel slightly at atmospheric temperature, although fruit juices containing an equal amount of the acid are generally quite free from any such action.

The higher chromium stainless irons have a reasonable resistance to cold solutions of the acid and also to very dilute solutions when hot, but they are attacked by more concentrated hot solutions. Some typical results appear in Table CVI.

TABLE CVI.

Action of Citric Acid on Stainless Irons.

(Rates of attack in grams per sq. m. per hour.)

Analysis of Iron.			Temp-erature of Test.	Concentration of Acid.			
Carbon %	Chromium %	Nickel %		5%	10%	25%	50%
0·10	15·5	0·39	15°C.	nil	1·10	2·42	2·93
			40°C.	6·04	4·62	11·1	10·8
			80°C.	34·6	54·2	69·1	50·7
0·10	17·9	0·28	15°C.	nil	nil	nil	nil
			40°C.	nil	0·46	1·0	0·41
			80°C.	nil	40·7	46·2	57·5

The austenitic chromium-nickel steels, containing 15/20 per cent. chromium and 12/7 per cent. nickel will resist the attack of solutions containing up to at least 50 per cent. acid at all temperatures up to and including boiling point. A solution saturated at 100°C. or higher, however, attacks all these steels quite rapidly—see Table CVII—although it

may be noted that passivity may occur, resulting in no attack, even under these severe conditions.

Commercial citric acid frequently contains small amounts of sulphuric acid; solutions of such impure acid attack the austenitic steels at boiling point quite rapidly, even if the sulphuric acid content be as low as 0·2 per cent. It should be noted, however, that passivity effects frequently arise with such solutions; a sample that has been attacked by exposure to the boiling impure acid may show no further effect on being exposed again to its action.

TABLE CVII.

Action of Citric Acid on Chromium-Nickel Steels.

(Rates of attack in grams per sq. m. per hour.)

Analysis of Steel				Concentration of Acid	
Carbon %	Chromium %	Nickel %	Temperature of Test	5% 10% 25% 50%	Saturated at 100° C
0·12	14·9	10·7	15°C.	nil	--
			40°C.	nil	-
			80°C.	nil	--
			boiling	nil	46·2
0·12	18·0	8·2	15°C.	nil	-
			40°C.	nil	--
			80°C.	nil	--
			boiling	nil	18·7

Cresylic Acid has no action on the high chromium irons or the austenitic steels, even at boiling point. Results of tests on such alloys are given in Table CVIII.

TABLE CVIII.

Action of Cresylic Acid on Stainless Steels.

Composition of Steel				Temperature of Test.
Carbon %	Chromium %	Nickel %	Molybdenum %	15°, 40°, 60°, 80° C., and b.p.
0·07	15·7	0·16		
0·10	16·6	10·2	—	No action in any case
0·18	17·2	10·1	3·42	

Formic Acid is distinctly more corrosive than . acetic acid. The austenitic chromium-nickel steels possess a reasonable resistance to solutions of this acid at atmospheric temperature but they are readily attacked by hot solutions. The pure acid (100 per cent.) is much less corrosive than its aqueous solutions. The best resistance appears to be obtained with chromium-nickel-molybdenum steels, see Table CIX; these, however, are attacked at boiling point or at somewhat lower temperatures.

TABLE CIX.

Action of Formic Acid on Stainless Steels.

(Rates of attack in grams per sq. m. per hour.)

Composition of Steel.					Temp-erature of Test.	Concentration of Acid.				
Carbon %	Chro-mium %	Nickel %	Copper %	Molyb-denum %		1%	10%	50%	90%	100%
0·09	13·5	0·30	—	—	15°C.	1·64	12·1	15·8	0·23	nil
					40°C.	3·94	51·0	43·4	2·85	0·03
					60°C.	- -	80·7	216	11·1	0·15
0·07	15·7	0·16	—	—	15°C.	nil	4·3	4·4	0·14	nil
					40°C.	2·61	23·7	31·5	0·55	nil
					60°C.	2·93	44·1	126	8·5	nil
0·10	15·2	11·4	—	—	15°C.	nil	0·07	0·24	0·14	nil
					40°C.	nil	0·77	1·64	0·60	nil
					60°C.	nil	3·15	11·1	1·12	0·14
0·12	18·0	8·2	—	—	15°C.	nil	nil	0·88	nil	nil
					40°C.	nil	nil	2·69	0·56	nil
					60°C.	nil	2·37	13·4	1·0	nil
0·13	20·1	9·9	—	—	15°C.	nil	nil	nil	nil	nil
					40°C.	nil	nil	nil	nil	nil
					60°C.	nil	nil	8·8	nil	nil
					80°C.	nil	nil	21·4	10·5	nil
					b.p.	0·85	10·7	41·8	—	nil
0·10	17·8	10·1	2·20	—	15°C.	nil	nil	0·16	0·13	nil
					40°C.	nil	nil	0·45	0·55	nil
					60°C.	nil	1·20	2·82	0·93	nil
0·13	17·2	10·1	—	3·42	15°C.	nil	nil	nil	nil	nil
					40°C.	nil	nil	nil	nil	nil
					60°C.	nil	nil	nil	nil	nil
					80°C.	nil	nil	nil	1·35	nil
					b.p.	nil	2·24	4·49	2·52	nil

Lactic Acid.   Solutions of this acid attack the stainless irons even at atmospheric temperature, the rate of attack apparently increasing with dilution, as will be seen from the data in Table CX regarding material of this type ; raising the temperature to 40°C. increases the rate of attack considerably.

·   TABLE CX.

Action of Lactic Acid on Stainless Steels.

(Rates of attack in grams per sq. m. per hour.)

Composition of Steel.				Concentration of Acid.		
Carbon %	Chromium %	Nickel %	Temperature of Test.	5%	50%	100%
0·09	16·3	0·17	15°C.	1·21	0·72	0·17
			40°C.	11·2	8·47	1·79
0·14	16·8	10·5	15°C.	nil	nil	nil
			40°C.	nil	nil	0·27
			60°C.	nil	nil	0·87
			80°C.	nil	0·02	1·45
			b.p.	0·49	20·6	—

The austenitic steels resist its attack perfectly satisfactorily under such conditions but are attacked at higher temperatures, even by dilute solutions.   Thus Messrs. F. Krupp report that " V.2.A.," " V.4.A. " and " V.6.A." are all attacked at a rate of 1·0/3·0 grams per square metre per hour by a boiling solution containing 1·44 per cent. of the acid ; also, Messrs. T. Firth & Sons, Ltd., state that a sample of " Staybrite " was attacked at a rate of 1·67 grams per square metre per hour by a 50 per cent. solution at a temperature of 100°C.   Further data given in Table CX.

Lactic acid is, of course, present in sour milk ; but it does not follow that the latter material will attack the stainless irons in the same way as pure solutions of lactic acid.   The colloidal organic matter present in milk exercises a retarding action on lactic acid similar to that produced, for example, on acetic acid in vinegar.   Actually, the high chromium irons resist perfectly the attack of milk, sour or otherwise.

TABLE CXI.

Action of Oxalic Acid on Stainless Steels.

(Rates of attack in grams per sq. m. per hour.)

Composition of Steel.					Temperature of Test.	Concentration of Acid.	
Carbon %	Chromium %	Nickel %	Copper %	Molybdenum %		2½ %	Saturated at 15° C.
0·09	13·5	0·30	—	—	15°C.	0·64	1·64
					40°C.	2·49	5·14
					60°C.	8·28	27·8
					80°C.	30·7	40·5
					b.p.	35·0	110
0·07	15·7	0·16	- -	—	15°C.	0·05	0·31
					40°C.	0·25	1·01
					60°C.	0·42	8·73
					80°C.	18·5	35·3
					b.p.	52·9	93·4
0.08	20·7	0·23	—	—	15°C.	—	nil
					40°C.	—	nil
					b.p.	—	7·2
0·10	15·2	11·4	- ·	-	15°C.	0·09	nil
					40°C.	0·80	1·08
					60°C.	2·0	5·53
					80°C.	3·74	7·2
					b.p.	3·6	7·6
0·12	18·0	8·2	·-	—	15°C.	nil	nil
					40°C.	nil	0·25
					60°C.	0·63	2·02
					80°C.	1·58	4·73
					b.p.	3·27	5·46
0·13	20·1	9·9	—	--	15°C.	nil	nil
					40°C.	nil	nil
					80°C.	nil	nil
					b.p.	2·39	4·06
0·19	18·4	8·4	—	4·1	15°C.	nil	nil
					40°C.	nil	0·24
					60°C.	nil	0·25
					80°C.	nil	0·24
					b.p.	1·85	3·29
0·10	17·8	10·1	2·2	—	15°C.	nil	nil
					40°C.	nil	0·14
					60°C.	0·11	1·62
					80°C.	1·69	1·71
					b.p.	2·67	8·35

Oleic and other Fatty Acids have no action on stainless steel either· when cold or heated to about 100°C. At 150°C. a slight attack (0·18 grams per square metre per hour) was produced on a stainless iron containing 15·4 per cent. chromium, but even at this temperature, an austenitic steel (" Anka ") was quite unaffected.   Messrs. F. Krupp report that at 200°C., under two or three atmospheres pressure, V.2.A., ·V.4.A. and V.6.A. were " vollkommen beständig," this term signifying that their rate of attack (if any) was less than 0·1 gram per square metre per hour.

Oxalic Acid attacks stainless irons, especially when hot, though if the chromium content be raised to at least 20 per cent., no attack is produced at temperatures up to 40°C.   The austenitic steels are satisfactory at atmospheric temperature—a high chromium content is also an advantage here—but they are attacked by hot solutions.   Somewhat better results are obtained from molybdenum-containing steels, but addition of copper appears to have only a slight effect ; see Table CXI.   It may be noted that the oxalates, formed as a result of attack on the various steels, are sparingly soluble salts ; hence the manner of their deposition on the steel, and the adherence or otherwise of the deposit, are likely to affect considerably the further action of the acid on the steel.

Tannic Acid.   The results of tests on mild steel and on three typical varieties of stainless steel are given in Table CXII.   The solution in contact with the 12/14 per

TABLE CXII.

Action of Tannic Acid on Ordinary Mild Steel and on Stainless Steels.

(Rates of attack in grams per sq. m. per hour.)

Composition of Steel			Concentration of Acid	Temperature of Test.	
Carbon %	Chromium %	Nickel %		15° C.	80/85° C.
0·26	—	—	10%	0·04*	0·92*
0·80	12·6	0·79	,,	nil	0·019†
0·08	15·4	0·80	,,	nil	nil
0·10	15·2	11·4	,,	nil	nil

* Solution turned black as ink.

† Solution darkened slightly.

cent. chromium steel at 80/85°C. was darkened slightly, but no change in colour was observed in the solutions in any of the other tests on the stainless steels. The solutions in which the ordinary mild steel was placed rapidly turned black as ink.

Tartaric Acid attacks stainless irons distinctly at atmospheric temperature and rapidly when hot. The austenitic steels give much better results, but a content of at least 18 per cent. chromium is necessary if resistance to boiling solutions of moderate concentration is desired. All such steels, however, even with as high a chromium content as 21/22 per cent., are rapidly attacked by a boiling solution

TABLE CXIII.

Action of Tartaric Acid on Stainless Steels.

(Rates of attack in grams per sq. m. per hour.)

Composition of Steel.					Concentration of Acid.				
Carbon %	Chromium %	Nickel %	Molybdenum %	Temperature of Test.	1%	5%	25%	50%	Saturated at b.p.
0·09	13·5	0·30	—	15°C.	0·83	2·76	3·12	6·0	—
				40°C.	2·67	11·0	22·8	33·8	—
				b.p.	—	90·5	246	69·8	—
0·09	16·1	0·17	—	15°C.	nil	0·6	1·15	1·46	—
				40°C.	nil	2·84	5·47	6·47	—
				b.p.	—	17·7	127	68·6	—
0·12	14·9	10·7	—	15°C.	nil	nil	nil	nil	—
				40°C.	nil	nil	nil	nil	—
				b.p.	—	nil	11·0	21·8	9·8
0·10	17·1	8·1	—	60°C.	—	nil	1·2	1·88	—
				b.p.	—	nil	15·2	16·6	—
0·12	18·0	8·2	—	15°C.	nil	nil	nil	nil	—
				40°C.	nil	nil	nil	nil	—
				b.p.	nil	nil	nil	nil	18·9
0·14	21·3	11·0	—	15°C.	nil	nil	nil	nil	—
				40°C.	nil	nil	nil	nil	—
				b.p.	—	nil	nil	nil	14·6
0·13	17·2	10·1	3·42	15°C.	nil	nil	nil	nil	—
				40°C.	nil	nil	nil	nil	—
				b.p.	—	nil	nil	nil	0·65

saturated at boiling point. An addition of molybdenum to the steel produces a distinct improvement in the resistance to the boiling concentrated solution, but immunity from attack is not attained; see Table CXIII.

Fatigue and Corrosion-Fatigue. The problem of the strength of materials under alternating or repeated stresses is of the utmost importance in certain branches of engineering work; its importance is, frequently, increased considerably when corrosion takes place simultaneously with the alternating or pulsating stresses.

It has been known for many years that a stress which would cause no apparent damage to a metal part if applied once or a few times, might cause failure if repeated a very large number of times. Similarly, failure might occur if the stress alternated rapidly between positive and negative values (i.e. alternate tension and compression) during a considerable period of time. The failure of metals under such repeated or alternating stresses has been known under the general name of " fatigue " and many investigations have been carried out to determine the maximum range of stress which could be applied indefinitely to specific metals without causing failure. For many years it was considered that the elastic limits in tension and compression represented the maximum stresses to which metals could be submitted without fatigue, and hence the value of the elastic limit in tension (that in compression being similar in normal metals) was looked upon as the criterion of fatigue-resisting properties. Investigations carried out during the last fifteen or twenty years, by the Air Board in this country (*), by Prof. Moore and his associates at Illinois (†), by Dr. McAdam (‡) and by others, have shown that there is no apparent connection between the elastic limit in tension (or the yield point for that matter) of a metal and its fatigue range. On the contrary, the only value given by the tensile test which showed any regular relation to the fatigue range was the maximum stress, and this relation was only approximate.

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* " Report on the Materials of Construction used in Aircraft and Aircraft Engines." H.M. Stationery Office. See also " Fatigue in Metals." H. J. Gough.
† " An Investigation of the Fatigue of Metals." H. Moore, J. B. Kommers, and T. M. Jasper. *Eng. Exptl. Station, Univ. of Illinois., Bulletins Nos. 124, 136, 142, 152.* See also " The Fatigue of Metals." H. Moore and J. B. Kommers.
‡ " Endurance of Steel under Repeated Stresses." D. J. McAdam. *Chem. and Met. Eng.,* December 14th, 1921. " Endurance Properties of Steel." D. J. McAdam. *Proc. A.S.T.M.,* Vol. XXIII, Pt. 2, p. 56 (1923).

These investigations showed that in the case where the stress alternated between tension and compression values of the same magnitude, the maximum value to which this stress could be raised without the steel exhibiting evidence of fatigue was 45 to 50 per cent. of the maximum stress in tension. This value is generally known as the " fatigue " or " endurance " limit. While the relationship mentioned above held for quite a number of metals, it was not universally true ; there were exceptions, notably among metals other than iron and steel. As an indication of the type of agreement found among ferrous metals, however, the results given in Table CXIV are taken from the Air Board publication mentioned earlier :—

TABLE CXIV.

Fatigue Ranges of Various Steels.

Material.	Elastic Limit, tons per sq. inch.	Max. Stress, tons per sq. inch.	Fatigue Limit, tons per sq. inch.	Ratio of Fatigue Limit to	
				Elastic Limit.	Max. Stress.
Case hardening steel	17·6	39·5	±18·4	1·04	0·47
,, ,, ,, 3% nickel	16·0	65·5	±31·0	1·94	0·47
,, ,, ,, 5% ,, ...	14·0	60·0	±30·0	2·15	0·50
,, ,, ,, 6% ,, ...	20·0	57·8	±26·5	1·32	0·51
Air hardening nickel chrome steel, hardened ...	20·0	109·1	±45·5	2·28	0·42
,, ,, ,, ,, ,, temp. 200°	36·2	101·2	±51·5	1·42	0·51
,, ,, ,, ,, ,, ,, 400°	53·3	97·9	±47·5	0·89	0·49
,, ,, ,, ,, ,, ,, 500°	51·7	82·4	±41.5	0·80	0·50
,, ,, ,, ,, ,, ,, 600°	40·9	70·1	±35·5	0·87	0·50
Nickel chrome steel, oil hardened and tempered	55·0	65·7	±33·0	0·60	0·50
Chrome vanadium steel, hardened and tempered	44·8	62·9	±32·8	0·73	0·52
Mild steel, normalised	23·1	37·9	±17·0	0·74	0·45
,, ,, hardened and tempered ...	25·4	46·8	±19·0	0·75	0·41
,, ,, cold worked	18·2	40·8	±19·1	1·05	0·46
,, ,, ,, ,, temp. 250° ...	20·5	40·1	±18·4	0·90	0·46
,, ,, ,, ,, ,, 400° ...	28·1	39·9	±19·0	0·68	0·48
,, ,, ,, ,, ,, 550° ...	25·0	36·8	±18·0	0·72	0·49

It will be seen from these tests that the ratio between fatigue range and maximum stress is fairly constant ; on the other hand, there is no apparent relation between fatigue limit and elastic limit.

Investigations as to the fatigue limits of various types of stainless steels indicate that these behave, in the main, in the same way as other ferrous metals. Some typical values are given in Table CXV and further data will be found in Table CXVI (page 396).

TABLE CXV.

Fatigue Ranges of Stainless Steel.

Carbon %	Chromium %	Nickel %	Copper %	Treatment	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Fatigue Limit, tons per sq. inch.	Ratio of Fatigue Limit to Maximum Stress.
0·12	12·1	—	—	Not stated ...	30·3	43·1	33·5	66·8	±21·5	0·50
0·09	13·2	—	—	Hot rolled ...	—	50·1	23·0	59·5	±21·4	0·43
0·08	11·78	—	—	O.H.985°, T.485° C.	15·5	74·4	18·0	58·5	±33·1	0·45
				,, T.540° C.	32·2	73·5	17·0	61·6	±34·4	0·47
				,, T.595° C.	?	49·0	20·5	70·0	±27·3	0·56
				,, T.705° C.	22·8	37·3	27·0	74·0	±20·1	0·54
				F.C.985° C. ...	9·5	28·3	40·0	72·0	±13·8	0·49
0·42	12·26	0·20	—	W.H.900°, T.540° C.	39·2	76·6	11·0	41·0	±39·3	0·51
				,, T.650° C.	37·0	54·3	15·0	52·2	±27·9	0·51
0·40	15·21	0·18	—	W.H.900°, T.485° C.	50·0	73·4	11·5	38·4	±37·8	0·51
				,, T.565° C.	?	55·1	13·5	48·3	±27·9	0·51
				,, T.650° C.	26·6	51·7	20·0	54·2	±26·6	0·52
				F.C.900° C. ...	21·2	49·1	28·0	61·4	±22·1	0·45
0·61	15·81	0·24	1·10	W.H.900°, T.485° C.	59·5	89·0	9·0	13·0	±51·2	0·57
				Annealed ...	22·4	44·6	28·0	46·5	±24·4	0·55
0·45	8·38	28·2	—	Not stated ...	23·5	49·6	24·0	48·9	±26·2	0·53
0·33	·8·31	19·7	—	,,	—	51·8	25·5	48·2	±24·6	0·48
					—	50·1	31·0	51·7	±24·6	0·49
0·16	17·32	8·10	—	,,	19·7	56·0	45·5	53·2	±22·3	0·40
				,,	22·4	59·4	47·0	56·3	±24·0	0·40
0·39	17·71	25·3	—	,,	22·8	51·5	22·5	34·9	±24·2	0·47
0·39	10·9	34·7	—	,,	29·3	50·2	29·0	46·6	±25·4	0·51

It will be noticed that only one steel of the " V.2.A." type is included among those listed in Table CXV; the results on two different bars of this material (of which, unfortunately, the heat treatment is not recorded), gave rather low values for the fatigue limit.   Dr. Hatfield* has obtained still lower results on a sample of " Staybrite " ; he quotes a fatigue limit of 17·0/17·5 tons per square inch on a fully softened piece of this material· which presumably would have a tensile strength of about 50 tons per square inch.

It has been found, however, that the fatigue strength of a metal is very appreciably affected if it be subjected simultaneously to alternating stresses and to corrosion. Apparently the first recorded observation on these lines was made in 1918 in this country and related to a remarkable series of fractures of railway carriage axles.†   Although broken axles had not been unknown, they had become rare prior to the date in question, when a number of axles fractured in rapid succession in the bogies of new carriages of one of the leading railways in this country.   Investigation showed that the fractures were all in one particular position relative to the carriage body—a position, it may be noted, where it had been unusual for fractures to occur—and that this particular position was exposed to spray from the lavatories on the carriages.   Although the axles were not appreciably corroded in the vicinity of the fractures, on the contrary they appeared to be cleaned by the spray, it was inferred that the latter had exerted some form of corrosive action.   The lavatory vents were accordingly rearranged so as to throw the spray clear of the axles and the carriages put back into service; they continued in use under normal traffic conditions without mishap.

The second case, also recorded by Prof. Haigh, occurred during the war.   In order to protect shipping against moored mines, contrivances called " Paravanes " or " Otters " were employed.   These were kite-like bodies which were attached by steel ropes to the stem of a vessel.   When the latter moved through the water, the paravanes—acting in a similar manner to kites—stretched out the towing ropes on each side of the vessel.   In this position, the ropes intercepted the moorings of mines with which they came into contact, first

* " The Development of Staybrite Steel."   Messrs. T. Firth & Sons, Ltd.

† " Chemical Action in Relation to Fatigue in Metals."   Professor B. P. Haigh. *Inst. Chem. Eng.*, March, 1929.

deflecting the mine from the vessel and finally severing its mooring. The towing ropes, however, were in a state of rapid vibration owing to eddies being formed round them in the water and, as a result, they rapidly failed by fatigue in an alarming manner. No improvement resulted from the use of thicker ropes or of steels of higher tensile strength but, as it was concluded that corrosive effects were being produced, protection of the wires by galvanising was tried. This immediately led to an increased endurance in the ratio of 8 or 4 to 1. When the wires were so protected, different qualities of steel revealed different endurances—a feature markedly absent in the case of unprotected wires—and actually the best results were obtained by using wire possessing a tensile strength of about 120 tons per square inch.

These results, however, were not published until 1929* and, meanwhile, the serious results attending the simultaneous application of corrosion and alternating stresses had been rediscovered, entirely independently, by Dr. D. J. McAdam. The latter while investigating the fatigue limits of various metals, had employed a stream of water for the purpose of cooling specimens tested under high stresses. The results obtained under such conditions, however, indicated that the corrosive action of the water had an extraordinary effect on the fatigue strength of steels. It is impossible† to

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* In 1917, Haigh published the results of some experiments on brasses in which the specimens, while under repeated stress, were subjected to the action of salt water, ammonia or hydrochloric acid. He found slight lowering of the fatigue resistance of Muntz metal and naval brass by the action of ammonia, but found no such lowering with other combinations of metal and corrosive agent.

† The following papers by McAdam may be consulted :—
    " Stress-Strain-Cycle Relationship and Corrosion-Fatigue of Metals." *Proc. A.S.T.M.*, 1926, Pt. 2.
    " Corrosion-Fatigue of Metals as Affected by Chemical Composition, Heat Treatment and Cold Working." *Trans. A.S.S.T.*, 1927, Vol. II, p. 355.
    " Corrosion-Fatigue of Non-Ferrous Metals." *Proc. A.S.T.M.*, 1927, Pt. 2.
    " Fatigue and Corrosion-Fatigue of Metals." Internat. Congress for Testing Materials. Amsterdam. Sept., 1927.
    " Corrosion of Metals as Affected by Time and by Cyclic Stress." *A.I.M.M.E.*, (Feb., 1928), *Tech. Pub. No. 58.*
    " Some Factors Involved in Corrosion and Corrosion-Fatigue of Metals." *Proc. A.S.T.M.*, 1928, Pt. 2.
    " Corrosion of Metals as Affected by Stress, Time and Number of Cycles." *A.I.M.M.E.* (Feb., 1929), *Tech. Pub. No. 175.*
    " Fatigue and Corrosion-Fatigue of Spring Material." *Amer. Soc. Mech. Eng.*, Dec., 1928.
    " Corrosion of Metals under Cyclic Stress." *Proc. A.S.T.M.*, 1929, Pt. 2.
    " Influence of Cyclic Stress on Corrosion." *A.I.M.M.E.* (Feb., 1930) *Tech. Pub. No. 329.*
    " The Influence of Stress Range and Cycle Frequency on Corrosion." *A.S.T.M.*, June, 1930.

give here an account of all Dr. McAdam's work, but it may be briefly stated that his results show :

(1) The corrosion-fatigue limit in fresh water of all carbon steels tested lies between about 7 and 11 tons per square inch, irrespective of their carbon content, heat treatment or tensile strength. The corrosion-fatigue limit of steels containing more than about 0·2 per cent. carbon appears to be somewhat lower in the hardened and tempered condition than in the annealed, notwithstanding the higher tensile strength and normal fatigue limit in the former condition.

(2) The first stage in corrosion-fatigue is probably the formation of a pit. If the pit is produced under an initial stress below the normal fatigue limit, its formation must be due to corrosion effects, though these are probably aided by the stress. As the pit progresses in depth, there is intensification of the actual stress at the bottom of the pit and, due to this, of the rate of its propagation by corrosion. The combined effects lead to the failure of the piece at an accelerated rate.

(3) It is highly probable that the rate at which corrosive effects are produced is accelerated by the simultaneous application of stress because experiments show clearly that if a test piece be exposed to corrosion in the absence of stress and then tested in fatigue, further corrosion being excluded, the effect on the fatigue strength is far less marked than if corrosion and stress are applied simultaneously. In the case of metals where protective films have an important bearing on resistance to corrosion, these effects of stress are understandable. Such a film is likely to be cracked, and its efficiency as a protective agency thereby impaired, if it be subjected to rapidly alternating stresses.

(4) The ordinary structural alloy steels appear to be no better than carbon steels. For example, a steel containing 0·4 per cent. carbon and 3·1 per cent. nickel, was hardened and tempered to give a tensile strength of 112 tons per square inch and was then found to have an

ordinary fatigue limit of 47 tons per square inch. Its corrosion-fatigue limit, when tested in fresh water, was rather less than 6 tons per square inch. The rapidity with which this steel was affected may be illustrated by the fact that when tested in water at 47 tons per square inch—a stress under which, apart from corrosive effects, it would last indefinitely—it broke in half an hour.

(5) The corrosion-fatigue limit of stainless irons and steels containing 12/20 per cent. chromium appears to lie between about 13 and 18 tons per square inch ; the value probably rises slightly with the chromium content in this range. A further increase to 27 per cent. chromium did not increase the corrosion-fatigue limit appreciably, but this may be due to the low tensile strength of the high chromium alloy.

(6) The austenitic chromium-nickel steels are still more resistant, giving values of 20/23 tons per square inch. Obviously, however, these high values can only occur in alloys whose normal fatigue limit is at least as high as this.

(7) The corrosive effects of sea water are considerably greater than those of fresh water. The data available is rather meagre but it suggests that the ordinary stainless irons and steels (12/14 per cent. chromium) have a corrosion-fatigue limit in seawater of about 6/8 tons per square inch, though a few rather higher values have been obtained. The austenitic alloys give values of about 12/15 tons per square inch,

A summary of McAdam's results will be found in Table CXVI. It is obvious that these results are of very considerable importance to designers of engineering structures, particularly in chemical plant, which are to be subjected simultaneously to alternating stresses and corrosion. The safe working stresses in such cases are low, but they are appreciably greater in the case of stainless steels, especially the austenitic type, than in either carbon steels or the ordinary alloy steels widely used now-a-days for engineering purposes.

TABLE CXVI.

Fatigue and Corrosion-Fatigue Limits of Various Steels.

No.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Copper %	Vanadium %
(1)	0·24	0·01	0·57	—	—	—	—
(2)	0·32	0·21	0·60	—	3·47	—	—
(8)	0·47	1·58	0·87	0·82	8·11	—	—
(4)	0·46	0·24	0·69	0·88	—	—	0·14
(5)	0·10	0·29	0·34	18·8	0·51	—	—
(6)	0·12	0·18	0·40	12·67	0·45	—	—
(7)	0·11	0·15	0·34	12·9	0·11	—	—
(8)	0·14	0·64	0·46	17·09	0·01	—	—
(9)	0·19	0·55	0·31	20·94	0·17	0·92	—
(10)	0·20	0·28	0·82	27·37	0·19	—	—
(11)	0·88	0·20	0·26	14·5	0·28	—	—
(12)	0·08	0·28	0·18	12·2	0·18	—	—
(18)	0·11	0·10	0·04	11·84	0·07	0·94	—
(14)	0·88	0·09	0·08	11·54	0·08	0·84	—
(15)	0·18	0·22	0·05	18·35	0·08	0·45	—
(16)	0·09	0·10	0·07	18·76	0·12	0·16	—
(17)	0·09	0·10	0·29	15·09	0·15	—	—
(18)	0·24	0·27	0·51	20·48	0·25	0·67	—
(19)	0·16	0·44	0·28	17·3	8·19	—	—
(20)	0·88	2·36	0·71	15·9	15·9	—	—
(21)	0·89	0·14	0·66	17·7	25·8	—	—
(22)	0·89	0·15	1·10	10·9	34·7	—	—

Composition of Steel.

TABLE CXVI.—*Continued.*

Fatigue and Corrosion-Fatigue Limits of Various Steels.

No.	Treatment.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Fatigue Limit, tons per sq. inch.	Corrosion-Fatigue Limit (tons per sq. inch).	
						Fresh Water.	Sea Water.
(1)	W.H.900°, T.480°C.	35·2	26·0	68·1	16·6	7·3	—
	F.C.900°C. ...	24·9	39·0	59·7	10·7	7·6	--
(2)	W.H.790°, T.540°C.	56·0	21·5	65·8	30·9	11·2	—
	F.C.900°C. ...	41·4	30·0	58·5	22·0	13·0	—
(3)	O.H.815°, T.400°C.	112·0	8·5	46·5	48·5	5·7	...
	F.C.800°C. ...	61·5	22·5	46·4	29·1	10·2	—
(4)	O.H.860°, T.400°C.	80·2	14·0	47·8	35·0	7·3	—
	,, T.540°C.	65·6	16·5	54·4	31·0	7·3	—
	F.C.860°C, ...	44·2	28·0	53·8	18·8	9·8	—
(5)	W.H.985° T.540°C.	78·5	19·0	61·2	29·0	9·8	—
	,, T.595°C.	55·6	22·0	70·1	29·5	11·8	—
	,, T.650°C.	46·7	23·0	70·0	25·2	14·7	—
	F.C.875°C. ...	36·0	34·5	73·5	20·3	11·8	—
(6)	Hard'd and temp'd	50·2	23·5	66·8	24·0	17·5	—
(7)	Annealed	40·0	35·5	64·2	25·0	17·0	12·0
(8)	F.C.925°C. ...	39·2	29·0	61·3	21·0	19·5	11·5
(9)	Annealed	39·3	28·0	52·2	21·0	18·1	13·5
(10)	Annealed	36·2	28·0	57·0	19·5	17·5	13·5
(11)	O.H.985°, T.580°C.	80·0	13·0	40·2	39·4	14·3	—
	,, T.650°C.	52·6	21·0	52·3	23·8	16·8	12·1
	F.C.925°C. ...	42·2	30·0	61·3	23·2	16·1	16·1
(12)	F.C.985°C. ...	27·5	41·0	67·5	17·4	13·4	—
	W.H.985°,T.650°C.	40·4	26·5	74·8	21·8	18·8	—
(13)	F.C.870°C. ...	35·6	32·0	65·6	18·3	15·2	6·2
(14)	F.C.925°C. ...	43·5	28·0	59·5	23·2	15·6	—
(15)	W.H.985° T.650°C.	40·7	25·5	63·5	26·3	17·8	5·8
(16)	,, ,, ...	37·8	28·5	70·8	22·3	15·6	8·0
(17)	Not stated ...	45·8	25·5	59·0	—	14·7	—
(18)	,, ,, ...	49·5	22·5	41·5	—	21·4	—
(19)	,, ,, ...	56·0	45·5	53·2	22·3	22·3	11·2
(20)	F.C.925°C. ...	56·5	26·0	38·0	28·5	22·7	—
(21)	Not stated ...	51·5	22·5	34·9	24·2	20·1	15·2
(22)	,, ,, ...	50·2	29·0	46·6	25·4	18·3	9·8

HEAT RESISTING STEELS

HEAT RESISTING STEELS

, Very soon after stainless steel was used commercially for the manufacture of cutlery, it was noted that it scaled much less than ordinary steel when heated to the temperatures commonly used for heat treatment processes. The difference was apparent even at tempering heats ; for example " temper colours " could be produced on a polished surface of stainless steel, but generally a much higher temperature was needed for the formation of a given colour on this material than on ordinary steel. The colours noted below were produced on polished samples of hardened " cutlery " quality stainless steel heated to the temperatures indicated :

Temperature.			*Temper Colour.*
300°C.	...	...	Pale Straw.
350°C.	...	...	Brownish Straw.
400°C.	...	...	Brownish Purple.
450°C.	...	...	Bluish Purple.
500°C.	...	...	Reddish Purple.
550°C.	...	...	Purple Blue.
600°C.	...	...	Light Blue.
650°C.	...	...	Bluish Violet.
700°C.	...	...	Greyish Violet.
750°C.	...	...	Grey.

Temper colours are known to be due to interference effects produced by thin films of oxide on the surface of the steel. The thickness of the film so formed increases with rising temperature and in due course becomes sufficiently thick to be more or less opaque. Such a visible " scale " is produced on a 12 per cent. chromium steel at about 700°C. A polished surface of this steel, after being heated between 700°C. and 800°C., becomes covered with an adherent thin grey film, without however losing entirely its polished appearance, and the sample neither gains nor loses weight appreciably even after prolonged heating. Above about

825°C. however the steel begins to scale appreciably, the rate of oxidation increasing as the temperature rises.

A similar sequence of changes, though not necessarily at the same temperatures, probably occurs when most metals, including heat resisting steels, are in contact with hot oxidising gases. The differences in their behaviour, as regards temperatures necessary to produce similar effects, would seem to be due to the protectiveness or otherwise of the oxidation skin, or temper colour, first formed on their surfaces. If this skin be non-porous and tightly adherent, it is likely to protect the metal underlying it and hence prevent further oxidation ; on the other hand, a porous or loose skin will have no similar protective effect and hence will grow in weight and thickness. The latter conditions are typical of ordinary steel, for example ; the former are what should characterise a heat resisting alloy. At temperatures up to about 800°C., the oxidation film formed on 12/14 per cent. chromium steel is highly protective. At higher temperatures it gradually loses this characteristic ; it thickens more rapidly and becomes less adherent. The steel enters what may be termed its " free scaling " range.

The comparative behaviour of stainless steel and other types of steel on prolonged heating at high temperatures is illustrated in Fig. 192. In this experiment, samples of various steels, in the form of cylinders about ⅝ inch diameter and weighing 60 grams, were heated together in a gas-fired furnace. The temperature of the furnace was raised after definite periods of time as shown in the diagram. At the end of each 24 hours, the samples were drawn from the furnace and, after the loosely adherent scale had been removed, were weighed. The loss in weight is shown as a percentage of the original weight. It will be seen that after being held for seven days in the range 700°/825° C. the sample of stainless steel had hardly altered in weight, the actual loss being 0·25 per cent. On the other hand; the mild carbon steel and the ordinary types of structural alloy steels had lost amounts varying from 17 to 22 per cent. of their weight after the same treatment. The high speed steel lost 7·1 per cent. of its weight and the 25 per cent. nickel steel, which most nearly approached the stainless steel, 2·6 per cent.

The resistance of stainless steel to scaling at temperatures up to rather more than 800° C. led to its second

important commercial application, namely the manufacture of exhaust valves for internal combustion engines. Its use for this purpose assumed very considerable proportions during the Great War, particularly in connection with aeroplane engines; it led in fact to the whole supply of the steel in this country being taken by the Government for war purposes.
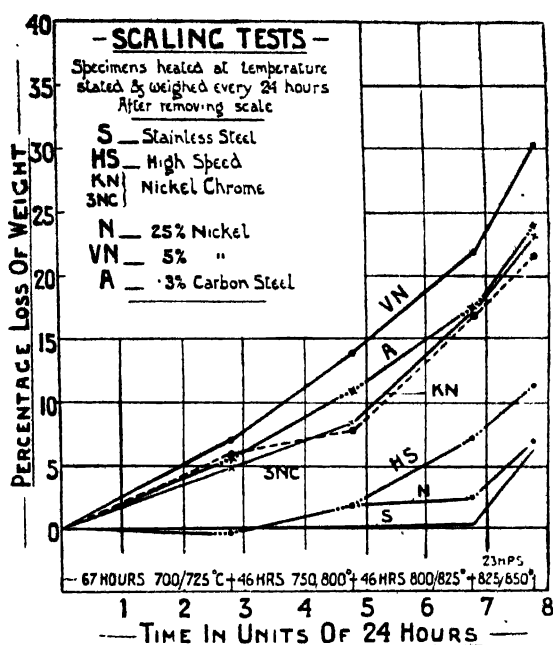
FIG. 192. Scaling tests on stainless and other steels.

Since that time demands for steels for use at high temperatures have become more and more insistent and have been met, with greater or less success, by that product of the last decade " heat resisting steel."   Prior to this period such special equipment as was required to possess the property of stability at high temperatures, had been manufactured from nickel-chromium-iron alloys of the " nichrome " type. These alloys, however, were very expensive and hence were only employed where operating conditions precluded the use of less resistant metals.   Thus they were used for such equipment

as electric heaters, thermocouples and special· parts of furnaces. As a rule, however, the engineer was content to use much cheaper and less resistant material, e.g. cast iron, design his equipment on a generous scale and replace it at frequent intervals. In the special equipment mentioned above, the property desired in the material was, generally speaking, resistance to oxidation. Recently, however, the demands of the engineer have widened considerably and the modern heat resisting alloy is frequently called upon to be immune from the attack of various corrosive gases at high temperatures and to possess, while so heated, a considerable degree of strength and resistance to deformation. These diverse requirements are not always equally satisfied by specific alloys; for example, two materials of different composition may be equally good in their resistance to oxidation at high temperatures but may possess widely different strengths while so heated. It will be useful, therefore, to consider first resistance to oxidation as a function of composition, and afterwards, the relative strengths of different alloys.

At low temperatures, a polished surface of high chromium steel commences to colour slightly at 200/300° C., depending

<div align="center">TABLE CXVII.</div>

Temper Colours formed on Stainless Steels.

Composition of Steel.			Colour formed after 1 hour at			
Carbon %	Chromium %	Nickel	200° C.	300° C.	400° C.	450° C.
0·09	16·0	0·34		Straw	Bronze	Blue
0·10	20·4	0·80	No	,,	,,	Blue-bronze
0·10	24·4	0·37	visible	Faint straw	Dark straw	Bronze
0·19	38·4	0·36	colour	,,	Straw	Dark straw
0·10	15·2	11·4		Straw	Bronze	Blue
0·12	18·0	8·2		··	,,	,,

on composition. The higher the chromium content, the higher the temperature at which colour becomes visible, but even with 38·4 per cent., an appreciable tint was produced on a polished sample after heating for one hour at 800° C. An indication of the effect of composition will be found in the

results of the tests detailed in Table CXVII. The polished samples to which these tests refer were held for the periods mentioned in an electrically heated muffle furnace.

TABLE CXVIII.

Oxidation Tests on Steels.

Samples heated for twenty-four hours in air.

Temperature.	Index Figure.		
	Mild Steel— 0·17% Carbon.	Chromium Steel— 0·32% Carbon, 13·12% Chromium, 0·29% Nickel.	Chromium-Nickel Steel— 0·12% Carbon, 17·74% Chromium, 8·06% Nickel.
100° C.	nil	nil	nil
200° C.	0·03	0·01	nil
300° C.	0·13	0·04	0·02
400° C.	0·45	0·08	0·04
500° C.	0·62	0·09	0·04
600° C.	4 64	0·20	0·18
700° C.	11·92	0·40	0·22
800° C.	44 92	0·77	0·40
900° C.	57·17	1·07	0·46
1000° C.	135·78	66·67	21·82
1100° C.	208·00	165·27	72·80
1200° C.	899·88	261·00	177·66

Figures giving increase of weight due to heating at different temperatures were obtained by Dr. Hatfield* and are quoted in Table CXVIII. The " index figure " in this table represents increase in weight in terms of milligrams per square centimetre of surface.

The formation of these oxide films on high chromium steels at comparatively low temperatures is of importance in the wire and strip industry because, owing to their content of chromium, the films are not reducible again to metallic form by hydrogen or coal gas at temperatures up to at least 1,000° C. In the ordinary method of bright annealing, as applied to carbon steels and to copper and many of its alloys, the wire or strip is placed in closed pots and heated up to the temperature required. The small amount of air in the box expands on heating and much of it escapes through a valve

*J.I.S.I., 1927, I, p. 481.

in the lid before the wire or strip becomes sufficiently hot to suffer any great oxidation.   Some of it is also displaced by grease with which the metal may have been coated and which is vaporised at low temperatures.   The small amount of air which remains in the box when the contents reach a red heat only produces a tarnish on the surface of the wire or strip. On withdrawing the box from the furnace, the air remaining in it is displaced by coal gas, a stream of which is passed slowly through the box until the latter and its contents are cold.   The coal gas reduces the oxide on the surface of the wire and hence removes completely the tarnish produced during heating, a bright surface being thereby obtained on the metal.
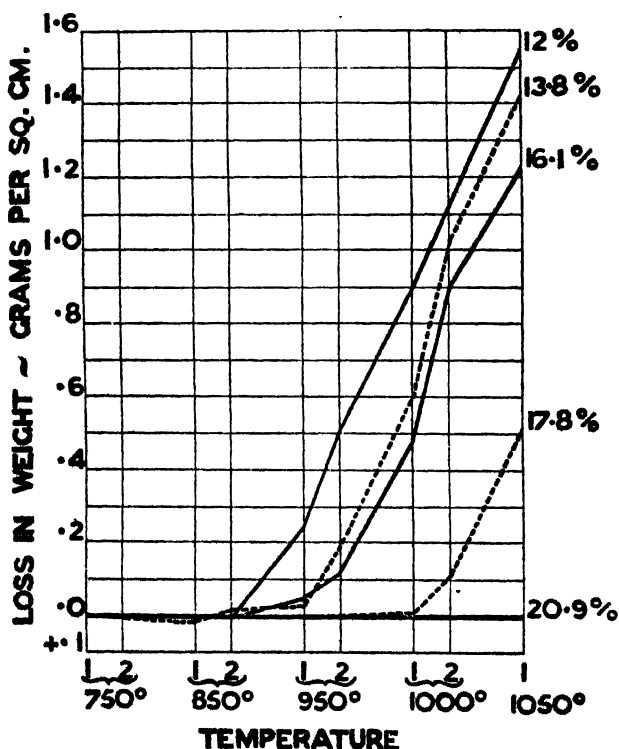
Fɪɢ. 193.   Effect of chromium content on the rate of scaling of stainless irons ; see page 407.

This method, however, fails completely with high chromium steels because the tarnish produced in the early

stages, although it may be considerably thinner than that
formed under similar conditions on ordinary steel is not
reduced by the subsequent treatment with coal gas ; hence
the wire or strip so treated remains tarnished.   The only way
of bright annealing the high chromium steel is to prevent the
temper colour forming, e.g., by completely replacing the air
in the box by pure hydrogen before the heating is com-
menced and maintaining the hydrogen atmosphere during
the whole time the steel is hot.

The onset of scaling, which occurs in 12 per cent.
chromium steel at 800°/850° C., may be delayed until higher
temperatures are reached by an increase in chromium content.
Fig. 193 for example, gives the results of tests on a series of
stainless irons, the samples (1 inch long and ⅝ inch diameter)
being heated in a gas-fired oven furnace (of such design that
the samples were surrounded by the products of combustion
of the gas) for two twenty-four-hour periods at 750° C.,
followed by two similar periods at each of the following
temperatures :   850°, 950°, 1,000° C.   Finally, they were
exposed for 24 hours at 1,050° C.   At the end of each period,
such loose scale as had been formed was removed from the
samples before they were weighed, but no attempt was made
to detach any that adhered tightly.   The curves show the
total losses in weight of each sample at the end of each
successive period.

TABLE CXIX.

Oxidation Tests on Chromium Steels at 950°/1,025° C.

Period :   10 days.

Composition of Steel.		Gain in Weight, %	Type of Scale.
Carbon %	Chromium %		
0·23	19·9	0·315	Thin adherent black scale.
0·23	24·8	0·03	Very thin greenish black scale.
0·24	28·1	0·01	Very thin adherent greenish scale.
0·19	33·4	0·02	

Steels containing about 20 per cent. chromium resist oxidation very well up to about 1,000° C., although they may scale to an appreciable extent after being held for prolonged periods at about this temperature. Still greater resistance may be obtained by a further increase in chromium content, as is indicated by the data in Table CXIX, relating to samples which were heated in a gas-fired oven furnace at 950°/1,025° C. for ten days.

Alloys containing 30 per cent. or so of chromium are extremely resistant even at considerably higher temperatures. Thus a further sample of the alloy containing 33·4 per cent. chromium (Table CXIX) was heated in a gas-fired furnace for 20 days at 1,000° C. (±25° C.) and then for 4 days at 1,100° C. At the end of this treatment, the sample was coated with a light greenish skin and had lost only 0·53 per cent. of its weight. To give some idea of the significance of this figure it may be mentioned that a piece of ordinary mild steel of similar size, which was placed in the furnace beside the high chromium alloy for the first 3 days at 1,000° C. (±25° C.) only, lost in that period 45 per cent. of its weight by oxidation.

Steel containing 26/30 per cent. chromium and up to about 2 per cent. carbon is used extensively for case hardening boxes or other parts of equipment for heat treatment operations and is giving exceedingly useful service at temperatures up to at least 1,050° C. Its production in the form of castings presents no difficulties and it has the merit of being relatively cheap compared with some other types of heat resisting alloys.

Reviewing such data as is available, it would appear that straight chromium steels may be usefully employed, so far as resistance to oxidation is concerned, at temperatures up to certain maxima which are related to chromium content in the manner indicated below :—

Chromium %	Maximum temperature for use.
15	800°/850° C.
20	950°/1,000° C.
25	1,050°/1,100° C.
30	1,100°/1,150° C.

The figures here given refer to continuous or intermittent exposure over considerable periods of time.

Many commercial heat resisting steels are complex alloys containing, in addition to chromium, one or more of the following metals: silicon, aluminium, nickel, tungsten, copper, molybdenum. Most, if not all, of these alloys have been evolved empirically and, owing to the meagre amount of data available, it is difficult to assess the value of the various added metals in promoting resistance to oxidation. The results given in Tables CXX—CXXII* provide some interesting comparisons between various steels. The first of these

TABLE CXX.

Oxidation Tests at 750°/1,050° C.

The samples were held at each of the temperatures indicated, and each " period " was of 24 hours duration.

Figures marked " + " represent gain in weight, the others loss in weight. Both are expressed in milligrams per square centimetre of surface.

Mark.	Carbon %	Silicon %	Chromium %	Nickel %	Tungsten %
A	0·09	0·22	16·1	0·18	—
B	0·12	0·16	15·9	10·7	—
C	0·24	0·36	16·7	8·1	—
D	0·24	0·36	15·4	11·5	3·65
E	0·22	1·95	16·1	10·9	3·8
F	0·40	2·35	17·3	26·8	—

Mark.	Loss, or gain, in weight.								
	750° C.		850° C.		950° C.		1,000° C.		1,050° C.
	1st Period.	2nd Period.	1st Period.	2nd Period.	1st Period.	2nd Period.	1st Period.	2nd Period.	1st Period.
A	+0·2	+0·2	0·0	4·8	38·	114	470	900	1220
B	+0·6	1·2	3·9	5·8	92	207	465	670	940
C	+0·1	1·8	4·5	4·7	20	124	470	720	1090
D	+0·4	1·4	7·9	9·1	108	326	800	1225	1700
E	+0·1	0·1	0·1	0·1	3·8	78	52	182	536
F	+0·25	+0·2	0·0	0·25	0·8	1·6	3·0	5·9	8·8

* In the experiments to which these tables refer, loose scale was removed from the samples before their change in weight was determined, but no attempt was made to detach tightly adhering scale.

tables refers to tests carried out in the same manner as those plotted in Fig. 193. A comparison of steels A, B and C suggests that the addition of 8 or 10 per cent. nickel to a steel containing 16 per cent. chromium, or thereabouts, has little effect on its resistance to oxidation. The chromium content of steel D is somewhat lower than of B or C, but, even allowing for this, it is obvious that the 3 or 4 per cent. tungsten which this steel contains has not increased its resistance to oxidation. On the other hand, the further addition of

TABLE CXXI.

Oxidation Tests at 950°/1,000°C.

Mark.	Carbon %	Silicon %	Chromium %	Nickel %	Tungsten %
A	0·10	0·36	15·5	0·39	—
B	0·12	0·16	15·9	10·7	—
C	0·12	0·30	18·0	8·2	—
D	0·29	0·48	17·7	9·73	1·64
E	0·43	2·59	16·9	26·5	—
F	0·10	0·37	24·4	0·37	—
G	0·22	0·47	23·1	9·0	—
H	0·27	0·56	23·1	9·1	3·4
J	0·13	1·03	25·9	20·2	—
K	0·24	0·63	28·1	0·26	—
L	0·38	0·65	10·7	63·3	—

Mark.	Change in weight (gain marked +, other results represent loss) in milligrams per sq. cm. after		
	7 days.	15 days.	21 days.
A	980	—	—
B	401	—	—
C	457	—	—
D	925	—	—
E	3	3·2	18·8
F	+2·2	+1·6	3·0
G	1·2	58·0	98·5
H	1·4	13·0	58·0
J	+0·6	+0·25	0·4
K	1·0	0·6	2·6
L	+1·5	+1·4	+1·2

about 2 per cent. silicon to the chromium-nickel-tungsten steel has a very marked beneficial effect in this respect. The good results on steel F, containing about the same amount of silicon and chromium as E, but a much higher nickel content in place of the tungsten, should be noted.

Tests at 950°/1,000° C. and lasting for three weeks are summarised in Table CXXI. This range of temperature is above that at which steels containing 16 or 18 per cent. chromium, with or without 8/10 per cent. nickel, may be usefully employed and the samples A, B, C and D, referred to in this Table, were only included by way of comparison with the more resistant alloys. At the same time, the results on B and C suggest that the nickel which they contain has retarded somewhat the rate of oxidation in what may be termed the free scaling range of temperature although, as shown earlier, a similar amount of nickel does not appear to raise the temperature at which this type of oxidation commences nor to have any beneficial effect at such temperatures at which the chromium steel is resistant to scaling. The absence of effect under the latter conditions is also shown by comparing steels F and G which contain sufficient chromium to be reasonably resistant under the testing conditions selected for this experiment. On the other hand, a distinct improvement is noticeable when 20 per cent., or more, nickel is present ; see steel J, and compare also E with A—D. In passing, note that whereas steel D gives poor results, the tungsten content of H appears to show to better advantage than in the steels previously examined which contained this metal. The two remaining alloys, K and L, exhibit extremely good resistance to oxidation under the conditions described.

The effect of long continued exposure at 1,000°/1,100° C. on three alloys is given in Table CXXII. This range of temperature is about the highest at which steel B may be effectively · used, but the high chromium iron A behaves excellently, quite as well in fact as the alloy of the "nichrome" type.

The data given in the last three Tables suggest that the question of composition in relation to resistance to oxidation is not simple. The matter, however, becomes still more complicated if the effects of varying atmosphere be taken into account. The results given in the preceding pages were

TABLE CXXII.

Oxidation Tests at 1,000°/1,100°C.

Mark.	Carbon %	Silicon %	Chromium %	Nickel %
A	0·24	0·63	28·1	0·26
B	0·34	2·85	17·7	25·8
C	0·41	0·50	11·1	64·3

Mark.	Change in weight (gain marked +, other results represent loss) in milligrams per sq. cm. after					% Loss in weight.
	1 week.	2 weeks.	5 weeks.	14 weeks.	14 weeks, scale removed.	14 weeks scale removed.
A	4·3	2·0	3·1	10·9	20·6	0·72
B	3·4	15·2	69·5	88·5	97·0	3·4
C	+0·8	1·7	5·8	10·8	12·9	0·45

obtained by exposing the samples in a gas-fired furnace of the muffle type but fitted with an open tray instead of a closed muffle. The samples were therefore continuously exposed to the action of the products of combustion of the gas used (that distributed by the Sheffield Gas Co.) together with such air as was in excess of that required to burn the gas completely. Obviously, the oxidising effect of such a furnace atmosphere will vary with the purity of the gas used and with the amount of excess air. It is common knowledge that nickel alloys suffer much more oxidation when exposed to the products of combustion of a fuel of high sulphur content than when the latter element is present only in small quantity. As shown some years ago by Kayser[*] the bad effect of sulphur is due to the formation of an easily fusible eutectic of nickel and its sulphide.

A study of the relative effect of various " atmospheres " on the rate of oxidation of mild steel and a chromium-nickel steel was made by Dr. Hatfield,[†] whose results are given in

* Heat and Acid Resisting Alloys (Ni-Cr-Fe). J. F. Kayser. *Trans. Faraday Soc.*, XIX (1923), p. 184.

† *Loc. cit.*

Table CXXIII. Each test lasted 24 hours and the " index figure " represents the increase in weight of a sample expressed in milligrams per square centimetre of surface.

TABLE CXXIII.

Effect of " Atmosphere " on Rate of Oxidation, at 900° C.

Mark.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A	0·17	0·18	0·67	—	0·25
B	0·12	0·31	0·28	17·7	8·06

Condition of Atmosphere.	Index Figure.	
	Steel A.	Steel B.
Pure Air	55·24	0·40
Atmosphere	57·17	0·46
Pure Air + 2% SO_2	65·17	0·86
Atmosphere + 2% SO_2	65·76	1·18
Atmosphere + 5% SO_2 + 5% H_2O ...	152·42	3·58
Atmosphere + 5% CO_2 + 5% H_2O ...	100·44	4·58
Pure Air + 5% CO_2	76·88	1·18
Pure Air + 5% H_2O	74·21	3·24

These results indicate that furnace atmospheres containing considerable quantities of water vapour and either carbon dioxide or sulphur dioxide, are likely to cause a much greater amount of oxidation than air at similar temperatures. In an endeavour to assess the probable effects of such metals as are often found in heat resisting alloys, on the rate of oxidation of the latter by various gases, Dr. Hatfield also heated comparatively pure samples of half a dozen of these metals in different gases at various temperatures between 700° and 1,000° C. His results are summarised in Table CXXIV ; as before, each test lasted 24 hours and the "index figure " has the same significance as in Table CXXIII.

These results are worthy of study. Broadly speaking, it is evident that the order of resistance to attack by either oxygen, steam or carbon dioxide is the same, namely,

TABLE CXXIV.

Effect of Various Gases on Rates of Oxidation of Pure Metals.

Gas.	Metal.	Index Figure.			
		700° C.	800° C.	900° C.	1,000° C.
Oxygen	Iron ...	51·12	59·54	124·27	141·60
	Chromium...	0·47	0·97	2·24	6·31
	Nickel ...	0·96	1·15	2·82	9·69
	Cobalt ...	8·72	4·39	93·18	119·47
	Copper ...	11·97	19·08	48·95	—
	Tungsten ...	46·16	275·41	376·22*	—
Steam	Iron ...	62·24	84·71	57·53	178·39
	Chromium...	0·05	0·37	1·17	2·11
	Nickel ...	0·34	0·42	1·38	4·39
	Cobalt ...	0·81	0·82	25·90	78·55
	Copper ...	3·25	12·73	15·30	—
	Tungsten ...	2·08	17·70	179·21	—
Carbon Dioxide ...	Iron ...	58·74	72·25	113·27	175·
	Chromium...	0·27	0·34	1·33	3·08
	Nickel ...	0·39	0·87	3·56	4·56
	Cobalt ...	2·68	5·39	44·33	15·05
	Copper ...	6·55	9·89	12·56	—
	Tungsten ...	13·92	20·32	13·90†	—
Sulphur Dioxide...	Iron ...	35·42	79·10	Completely	converted
	Chromium...	0·16	0·39	3·25	3·57
	Nickel ...	92·28	366·73‡	83·73§	2·60‖
	Cobalt ...	59·77	102·79	163·30	289·82
	Copper ...	0·18	0·13	0·20	—
	Tungsten ...	47·05	72·78	29·00¶	—

chromium, nickel, cobalt, copper, iron, tungsten. The ease of oxidation of tungsten, particularly in oxygen and steam, ·should be specially noted ; also the marked acceleration in the rate of oxidation of cobalt as the temperature rises from 800° to 900° C.

The effects of sulphur dioxide differ notably from those

* Completely converted into WO_3.
† Oxide formed, but some volatilisation occurred.
‡ Scale disintegrated. ·
§ Scale firmly adherent.
‖ Scale very firmly adherent.
¶ Partial loss due to volatilisation.

of the other gases. Copper is here the most resistant—at least up to 900° C.—though chromium runs it very closely. On the other hand, nickel and cobalt are badly attacked ; the results at different temperatures with the former metal show anomalies which appeared to be connected with the character of the scale formed.

Having thus indicated the response of the individual metals, Dr. Hatfield tested in a similar fashion a number of steels and other alloys. His results on such of these as may be included in the category of stainless steels are given in Table CXXV, and a study of these indicates that the several steels are placed in much the same order of merit by oxygen steam or carbon dioxide. The result of an increase in chromium content from 14 to 18 per cent. may be seen by comparing steels B and C ; A indicates the protective effect of silicon, particularly at 900°/1,000° C., on a steel containing only about 9 per cent. chromium. The raising of the temperature at which marked oxidation occurs by an increase in chromium content, even in the presence of 8/10 per cent. nickel, is also evident from a comparison of steels D and E ; at the same time, the greatly increased resistance due to a much higher nickel content than this, even when combined with only 10/11 per cent. chromium, may be seen from alloys F and J. The two more complex alloys G and H are somewhat less easy to deal with ; the value of a high silicon content is evident however, from a comparison of G and E and one may at least surmise, in view of the results previously quoted, that the very satisfactory figures given by H are due to the silicon rather than to the tungsten it contains.

The results of the tests in sulphur dioxide, Table CXXV, present some anomalies not easy to explain. A comparison of steels C and E indicates that nickel is not useful, where this gas is concerned, at any temperature in the range 700°/1,000° C. A difference of the same order is observable between B and D at 700° C., but at 900° and 1,000° C. the nickel-bearing steel is much superior to the other ; the rather higher chromium content of D should however be kept in mind in this connection. The large amount of nickel in F appears, rather surprisingly, to have occasioned no bad effect at temperatures up to 900° C., although J, still richer in this metal, was distinctly attacked at 800° C.

TABLE CXXV.

Effects of Various Gases on the Rate of Oxidation of Steels.

Mark.	Carbon %	Silicon %		Chromium %	Nickel %	Tungsten %
A.	0·50	3·04	0·37	8·28	0·16	
B.	0·32	1·32	0·25	13·12	0·29	
C.	0·09	0·37	0·39	18·53	0·26	
D.	0·11	0·21	0·34	14·84	10·16	
E.	0·12	0·31	0·28	17·74	8·06	
F.	0·35	0·21	1·36	10·90	35·15	
G.	0·58	4·00	0·36	15·54	8·14	
H.	0·30	1·46	0·52	17·74	7·0	4·23
J.	0·06	0·71	0·89	11·69	60·40	
K.	0·17	0·18	0·67		0·25	

Gas.	Mark.	Index Figure.			
		700° C.	800° C.	900° C.	1,000° C.
Oxygen	A.	0·26	1·67	2·07	2·94
	B.	0·22	1·90	2·79	91·30
	C.	0·60	0·74	1·90	2·89
	D.	0·64	1·14	4·08	43·58
	E.	1·08	1·05	2·71	5·66
	F.	1·74	7·29	11·67	19·31
	G.	0·17	0·34	1·26	1·81
	H.	0·03	0·05	0·20	3·49
	J.	0·24	0·49	0·76	1·78
	K.	10·42	29·76	83·41	170·86
Steam	A.	0·34	0·54	0·95	1·36
	B.	0·52	0·57	14·91	39·84
	C.	0·24	0·58	2·03	3·26
	D.	0·47	1·88	19·94	43·44
	E.	0·24	0·50	6·14	17·46
	F.	1·31	2·04	6·15	16·03
	G.	0·10	0·27	0·93	1·50
	H.	0·10	0·31	0·37	2·77
	J.	0·23	0·30	1·41	1·43
	K.	3·66	21·97	74·93	231·05
Carbon dioxide ...	A.	0·25	0·21	0·43	0·84
	B.	0·81	0·87	16·05	62·28
	C.	0·24	0·76	2·89	2·95
	D.	1·43	2·09	12·41	37·01
	E.	0·39	1·08	3·25	5·85
	F.	1·05	2·21	7·33	11·65
	G.	0·12	0·22	0·55	0·58
	H.	0·15	0·15	0·32	0·92
	J.	0·41	0·44	0·55	1·13
	K.	10·03	36·74	74·92	93·46
Sulphur dioxide ...	A.	0·52	1·28	4·55	3·24
	B.	0·40	1·04	9·93	58·62
	C.	0·45	0·55	0·82	1·43
	D.	1·06	1·16	1·72	3·75
	E.	1·43	1·65	1·83	2·63
	F.	0·29	0·41	0·42	7·04
	G.	0·38	0·60	1·15	2·41
	H.	0·20	0·40	0·54	0·83
	J.	0·33	5·04	55·62	91·10
	K.	9·86	41·64	177·01	Converted

In the author's experience, at temperatures up to 700° C., a stainless iron containing 16·1 per cent. chromium (and 0·17 per cent. nickel) was distinctly better in its resistance to gas containing 7 per cent. sulphur dioxide than an austenitic steel containing 15·4 per cent. chromium and 10·8 per cent. nickel, the losses in weight after removing scale being respectively 0·018 and 0·08 grams per square metre per hour at 330° C. and 0·64 and 2·95 grams per square metre per hour at 700° C.

Apart from chemical processes, however, the engineer has rarely to deal with hot gases containing as much as 7 per cent. sulphur dioxide ; but he is frequently concerned with plant which is subjected to the hot products of combustion of impure fuels. These are likely to contain much less than 7 per cent. sulphur dioxide but, nevertheless, they may exert a very noticeable action on nickel-bearing steels. For example, a series of test samples of various heat resisting steels were placed in the flue of a large reheating furnace, fired with small coal, for a period of 16 working days. The temperature of the flue varied considerably during the test (it was generally 700°/800° C. but occasionally rose much higher, the maximum recorded being 1,100° C.), but as all the samples were exposed together under identical conditions, their behaviour is strictly comparable. At the conclusion of the

TABLE CXXVI.

Oxidation Tests in Flue of Coal-fired Furnace.

(Period : 16 days. Temperature : 600°/1,100°C.)

Composition of Steel.						Loss in weight (milligrams per sq. cm.).	
Carbon %	Silicon %	Chromium %	Nickel %	Tungsten %	Copper %	Loose scale removed.	All scale removed.
0·16	0·38	17·2	10·6	—	—	485	583
0·10	0·36	17·8	10·1	—	2·20	475	568
0·24	0·36	15·4	11·5	3·65	—	500	705
0·22	1·95	16·1	10·9	3·8	—	421	548
0·46	1·72	12·7	13·0	3·2	—	610	897
0·40	2·35	17·3	26·8	—	—	483	556
0·10	0·37	24·4	0·87	—	—	+31*	105

* This sample had gained in weight at this stage.

DD

test, loosely adherent scale was removed from the samples and their loss in weight determined; afterwards, the remaining, tightly adhering scale was detached by bending the samples slightly and then pickling them in 5 per cent. nitric acid, and the total loss in weight then determined. The results, set out in Table CXXVI, suggest that none of the steels containing up to about 18 per cent. chromium, together with 10 per cent. or more nickel, are particularly resistant under these admittedly rather severe conditions. Quite obviously, tungsten has no beneficial influence and the value of a high silicon content is less marked than in the previously recorded tests. The high chromium iron was much more resistant than the others; it may be noted that this sample pickled rather badly; hot acid was necessary to detach the scale and some metal was undoubtedly removed as well.

No determination was actually made of the sulphur content of the flue gas during the course of this experiment; probably the figure was at least 0·05 per cent. by volume, and may have been distinctly higher than this, but the conditions may at least be taken as typical of those produced by the combustion of ordinary commercial fuel. More precise determinations, from this point of view, were made by Dr. Hatfield. A series of steels were exposed at 900° C. to a " complex gas " having the composition given in column B below; this composition was selected empirically after examining the analyses of a number of flue gases. For comparison, a similar set of test pieces was exposed at the same temperature in an open muffle furnace fired by Sheffield gas (the conditions being similar to those in the author's experiments, see Fig. 193 and Tables CXX—CXXII); an analysis of gas extracted from this muffle during the course of the test is given in column A below.

	A	B
Nitrogen	67·7%	72·95%
Oxygen	1·34%	5·0%
Carbon dioxide ...	4·75%	12·0%
Steam	21·10%	10·0%
Sulphur dioxide ...	0·003%	0·05%
Carbon monoxide	5·10%	—

The results of the test are set out in Table CXXVII; each test lasted 24 hours and the " index figure " has the same significance as before, namely, increase in weight expressed

in milligrams per square centimetre. It will be noted that in almost every case a greater amount of oxidation is produced by the " complex " gas than in the ordinary muffle atmosphere.* The value of silicon in diminishing oxidation under the conditions of the experiments is strikingly evident, the results on steel B being especially worthy of attention. Even a smaller amount than the 8 per cent. present in this steel suffices to give very good protection to a steel containing

TABLE CXXVII.

Effect of Industrial Gases at 900° C.

Mark.	Composition of Steel.					Index Figure.	
	Carbon %	Silicon %	Chromium %	Nickel %	Tungsten %	Muffle Atmosphere	" Complex Gas "
A	0·17	0·18	—	0·25	—	73·10	80·23
B	0·50	3·04	8·28	0·16	—	0·51	0·84
C	0·32	1·32	13·12	0·29	—	20·50	18·32
D	0·09	0·37	18·53	0·26	—	1·38	1·25
E	0·11	0·21	14·84	10·16	—	3·84	6·00
F	0·12	0·31	17·74	8·06	—	0·33	2·70
G	0·35	0·21	10·90	35·15	—	1·01	2·53
H	0·24	0·16	0·09	36·90	—	27·7	30·06
J	0·58	4·00	15·54	8·14	—	0·06	0·69
K	0·30	1·46	17·74	7·0	4·23	0·18	0·43
L	0·06	0·71	11·69	60·40	—	0·77	1·40

only 6 or 8 per cent. chromium at temperatures up to about 800° C. For example, the results in Table CXXVIII indicate that a steel having this composition has adequate resistance at 700°/750° C., being nearly as good as 12/14 per cent. chromium steel under these conditions. Mathews† also refers to the beneficial effect of silicon on chromium-nickel steel of the " 18/8 " class. He mentions three such steels containing 0·4, 1·10 and 2·14 per cent. silicon, but otherwise similar in analysis, which were exposed for 36 hours at 980° C. ; after all scale had been removed from the samples, their losses in weight were in the ratio 22 : 12 : 1.

* It would also appear that the " complex gas " at 900° C. represents less severe conditions than obtained in the author's tests in the flue of a coal-fired furnace (Table CXXVI) ; possibly, in the latter test, erosion by dust in the flue gases had an appreciable influence on the results.

† *Ind. & Eng. Chem.*, Dec., 1929.

temperature acquires a protective skin, which afterwards retards oxidation considerably, its increase in weight per unit area and unit time is likely to be greater during these first few hours than afterwards. For this reason, two alloys which gave similar results in a short time laboratory test (e.g., of 24 hours' duration) might exhibit notable differences when exposed for long periods in practice if the oxidised skin formed on one had a distinctly greater protective value than that of the other. Obviously, however, the protective value of such a skin may be noticeably affected if the surface on which it is formed suffers abrasion under service conditions ; it may also be reduced if the steel is frequently cooled and then reheated instead of being exposed continuously at some given temperature. The difference in coefficient of expansion of steel and its oxide will tend to cause the latter to flake off during cooling and hence necessitate a new skin being formed on reheating. The tendency for flaking to occur varies to some extent among different steels, depending partly on their coefficient of expansion.

These considerations do not by any means suggest that laboratory tests are of little value in comparing heat resisting steels ; they indicate that, as in other forms of corrosion tests, it is difficult to reproduce service conditions in a laboratory. Materials may be sorted with considerable accuracy into their probable order of merit under works conditions ; there can be no doubt for example that of the test specimens shown in Fig. 195, samples A, B and C are likely to give much better service, than the other two, under practical conditions involving exposure to oxidising gases at about 1,000° C., but it is less easy to give an estimate of the probable service life of the three selected steels.

Summarising, it may be concluded that :—

(1) Chromium is the chief agent in promoting resistance to oxidation ; the amount of this metal required, in iron-chromium alloys to give protection at various temperatures is indicated approximately in the Table on page 408. The respective values are not affected appreciably by the presence of 8 or 10 per cent. nickel in the steel.

(2) A high nickel content, e.g., 20 per cent. or more, increases the protection afforded by a given amount of chromium to oxidation by air, oxygen, steam or carbon

dioxide.   A high nickel content, however, is not useful if resistance is desired at high temperatures to gases containing sulphur dioxide or other sulphur compounds.

(3) Small additions of silicon or aluminium, e.g., 1 or 2 per cent., increase very markedly the resistance of high chromium steels to oxidation.

(4) The presence of 3 or 4 per cent. tungsten in chromium or chromium-nickel steels does not appear to increase their resistance to oxidation.

Freedom from oxidation is not the only requisite of a heat-resisting steel.   Account must also be taken of possible changes in its structure, due either to prolonged heating at high temperatures or to repeated heating and cooling, and the effects these may produce on the physical properties of the steel while it is hot or after it has cooled down again to atmospheric temperature.

The plain chromium steels have a greater or less tendency, depending on their carbon and chromium contents, to harden on air cooling from high temperatures.   If an article of heat resisting steel is required to be repeatedly heated and cooled, it is not advisable that it should harden during these coolings because, if so hardened, it is much more likely to crack on being again reheated.   Consequently, when such service conditions are involved, it is not advisable to use steels, which have any marked tendency to airharden, at temperatures above their Ac.1 points, unless the rates of cooling which will occur in practice are definitely slow enough to prevent any noticeable hardening effect.   The contraction which takes place in steels on passing through the Ac.1 change should also be kept in mind ; articles of complex shape are liable to suffer distortion if they are unevenly heated through this change.

Apart from changes of phase such as occur at Ac.1 and Ar.1, the chief structural alteration produced in all metals due to prolonged heating at high temperatures is grain growth ; it may be well to consider this briefly.   Stainless irons and steels of the 12/14 per cent. chromium type consist, at temperatures below about 800° C., of ferrite grains through which particles of carbide are embedded more or less evenly. Grain growth in the ferrite may take place to some extent above about 600° C., but it is likely to be very slow, due to the obstructing effect of the particles of carbide.   These

carbide particles function in much the same way as the particles of thoria which are purposely added to tungsten which is to be made into electric lamp filaments. If the latter are made from pure tungsten, they may suffer rapid grain growth when in use and, as a result, become brittle and break easily. If however, about 0·25 per cent. of thoria (an infusible powder) is added to the tungsten, the particles of the former become evenly distributed through the grains of the latter, in which they are insoluble, and prevent them growing when the filament is hot. The result is a greatly enhanced filament life.

On prolonged heating at temperatures below Ac.1, the carbide particles in the 12/14 per cent. chromium steels gradually coalesce, forming fewer but larger particles. This coalescence occurs fairly rapidly above about 700° C., but at much slower rates at lower temperatures ; it may occur below 550° C., but a very long period would be required to produce any appreciable amount. The main effect of this " balling up " of the carbide is a reduction, to some extent, of the strength and hardness of the steel ; this will be referred to later.

800° C. is about the maximum temperature at which the 12/14 per cent. chromium steels resist scaling when in contact with oxidising gases ; hence possible structural changes which may occur in them, owing to long continued exposure at higher temperatures, are not important from the point of view of their use as heat-resisting steels. It may be mentioned, however, that the Ac.1 change occurs at about this temperature and that the austenite which is then formed hinders further grain growth in the ferrite.

The higher chromium steels are much more subject to grain growth, particularly if their carbon content be low. In irons containing 20 per cent. chromium, for example, the carbide generally exists as large particles, fewer in number than in the 12/14 per cent. chromium irons of similar carbon content. As a result, these particles have less obstructive action on the grain growth of the ferrite at temperatures above about 700° C. The tendency for grain growth to occur increases with temperature and as the 20 per cent. chromium iron may be used up to 950°/1,000°C., and, more-over, as the formation of austenite, due to the Ac.1 change, does not take place in this iron below about 900° C., the

opportunities for grain growth to occur during use are much greater than in the lower chromium irons. The high chromium material is likely to become exceedingly coarse grained on prolonged exposure at temperatures above 700°/800°C.   For example, Fig. 196 shows the fracture of the bar of 24 per cent. chromium steel used for the tests reported in Table CXXVI, after exposure for 16 days in the flue of a reheating furnace. The main part of the fracture consists of four large grains.   Similarly, Fig. 197 represents the structure of a pyrometer tube of steel containing 0·1 per cent. carbon and 20 per cent. chromium after 19 months' use in a reheating furnace at 850°/950° C. and indicates not only the large size of the ferrite grains but also the very marked coalescence of the carbide particles which has been produced. A grain growth such as is represented in these two photographs reduces still further the low toughness value which these high chromium steels normally possess.

Grain growth also occurs in the austenitic steels, but only to a notable extent at temperatures well above 1,000° C. Moreover, as these steels retain their toughness and ductility even when possessing very coarse structures, grain growth does not usually lead to trouble when the steels are used for heat resisting purposes.   Precipitation of carbide, owing to prolonged heating at temperatures below about 900° C. may, however, lead to considerable loss of ductility and toughness, both while the steel is heated and also after cooling down to atmospheric temperature.   Instances of the latter have already been given (see page 169) and reference to the changes in the properties of the heated material will be made later in this chapter.

Turning now to the question of the strength of metals at high temperatures, it may be said at once that however complex may be the subject of their resistance to oxidation by various hot gases, that of their permanence of dimensions under stress while heated is still more complicated.   The strength of metals while hot has become of paramount importance on account of modern tendencies to use higher and higher temperatures and greater and still greater pressures, both in steam plant and in many chemical processes.   The designer of equipment must have data as to the strength of the metals he proposes to use under the temperature conditions for which his equipment is designed.

Plate XLIV
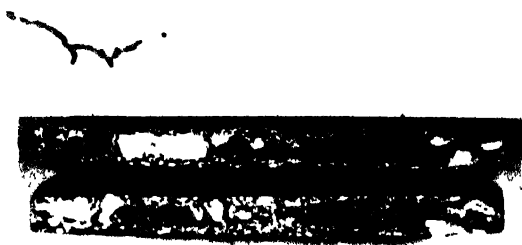
Fig. 196.   Fracture of bar containing 0·1 per cent. carbon, 24·4 per cent. chromium after 16 days in furnace flue, temperature 600–1,100° C.   × 1½.
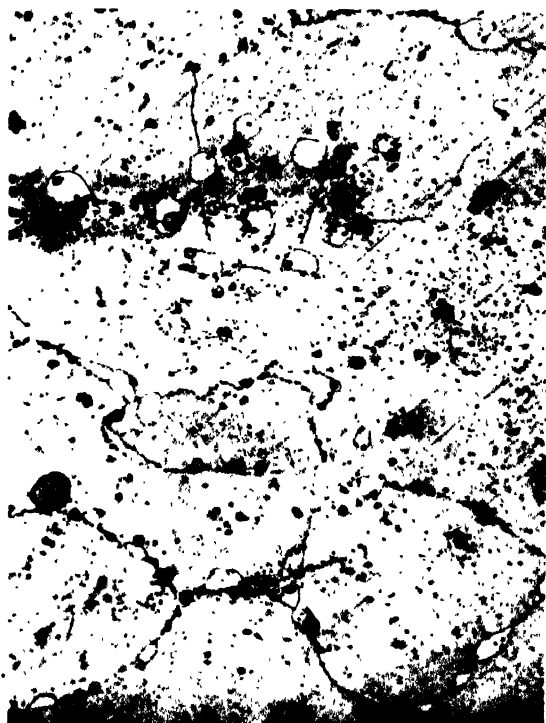
Fig. 197.   Structure of pyrometer tube (0·1 per cent. carbon ; 20·0 per cent. chromium) after 19 months' use in furnace at 850°/950° C.   × 100.

In the case of plant operating at atmospheric temperature — or not greatly above it—he has been accustomed for years to use the tensile strength of a metal as a basis for his calculations, and the experience of many engineers during the greater part of a century has indicated what fraction of this tensile strength he may regard as a safe working load. Hence, when the properties of metals at temperatures considerably above atmospheric first attracted attention, values for tensile strength at specified temperatures were determined in order to provide the required data.

The actual determination of the " tensile strength " of a metal at temperatures above atmospheric does not present any great difficulties. A test piece is placed in the jaws of a testing machine and is heated there in a suitably designed furnace to the required temperature. After holding at that temperature for a sufficiently long time to ensure uniformity, it is pulled while still hot and without removing from the furnace, the actual testing operation differing little from that on pieces tested under ordinary conditions. Numerous investigations into the properties of metals at high temperatures have been carried out in this way by different investigators. The values obtained may or may not be useful, but if obtained at temperatures above 300°/350° C., they certainly do not give the engineer data which he can use for designing purposes.

Unlike the values obtained from tests at atmospheric temperatures, those given by high temperature tests are influenced to a very great extent by the actual speed at which the test piece is pulled. That this was the case had been known for some time,* but it was scarcely realised to what extent heated steel behaved like a viscous fluid until Dickenson published the account of his remarkable investigations on the flow of steels at a red heat.† Dickenson showed that at temperatures of 500° C. and upwards (and later investigations indicate that the minimum may certainly be reduced to 400° C. and probably still lower), ordinary carbon steels and alloy steels of various types would stretch plastically and finally break under loads which were very considerably

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* See, for example, " Tenacity, deformation and fracture of soft steel at high temperatures," Rosenhain and Humfrey, *J.I.S.I.*, 1913, I, p. 219, and the discussion thereon by Dr. F. Rogers.

* † " Some experiments on the flow of steels at a red heat, with a note on the scaling of heated steels." J. H. S. Dickenson, *J.I.S.I.*, 1922, II, p. 103.

less than the figures for maximum stress obtained from carefully conducted tensile tests at the same temperatures. The gradual flow of heated metals under stress has been designated " creep " and since 1922 this subject has assumed a very prominent place in metallurgical and engineering literature and has led to a considerable amount of experimental work.   As a result, ideas as to the behaviour of
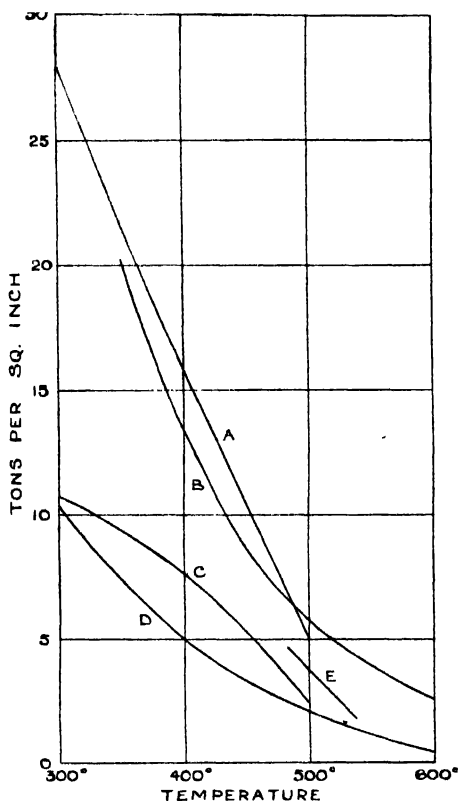
FIG. 198.   Values for " limiting creep stress " of mild steel, 0·2/0 24 per cent. carbon.

Curve A.   Tapsell and Clenshaw.
    „   B.   Cournot and Sasawaga.
    „   C.   Pomp and Dahmen.
    „   D.   French, Cross and Petersen.
    „   E.   Norton.

metals under stress at elevated temperatures are being clarified, though much still remains obscure.

If the results obtained by various workers are critically reviewed, however, their most notable feature is likely to be their variableness.   For example, all the curves in Fig. 198 relate to mild steel, containing 0·2/0·24 per cent. carbon, and they represent the values given by different investigators for the stresses with which this material may safely be loaded for long periods at the temperatures indicated.   The very great differences exhibited between these curves may well alarm the designer of high temperature equipment and raise doubts in his mind as to the value of the results placed at his disposal.

Actually this variableness is not really surprising.   The determination of a " limiting creep stress " (if such a thing really exists at temperatures of 400° C. and upwards) depends ultimately on the sensitiveness and accuracy of the means available for measuring the constancy in length of a given sample while it is heated to these temperatures.   If a number of test pieces of a given steel are loaded to different amounts at some given temperature, and the relation between extension and time determined in each case over a considerable
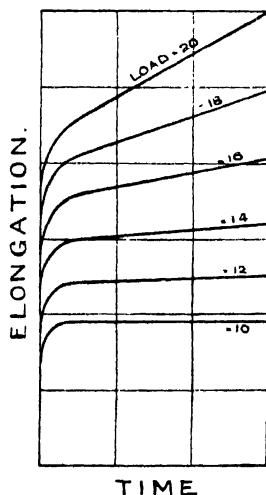
Fig. 199.   Relation between elongation and time ; metal strain hardens.

period, the curves representing this relation will be of one of two classes, depending on whether the temperature in question is above or below that at which the steel ceases to exhibit

strain hardening effects.   Consider for a moment a test piece
at a temperature at which the steel is still capable of harden-
ing distinctly when strained and suppose it to be loaded with
a stress sufficiently high to cause immediate plastic flow.
The relationship between extension and time for such a test
piece will be as indicated in the uppermost curve in Fig. 199.
The load being applied, the test piece immediately extends,
as shown in the diagram, and as a result, hardens.   Due to
this, the rate of extension diminishes and, after an interval,
assumes an apparently constant value.   If the test is re-
peated with gradually decreasing loads, both the amount of
initial extension and the subsequent steady rate of flow are
reduced and ultimately the latter is assumed to become zero
at some given load which has been named the " limiting
creep stress."   A set of curves produced in this way is
typified in Fig. 199.

On the other hand, if the testing temperature be raised
to a value at which strain hardening effects cease to be pro-
duced in the steel,* conditions are rather different.   In this
case it is difficult to see how a rate of creep once set up in the
material can ever become zero though, owing to viscosity,
it may possess an exceedingly small value.   On this basis,
therefore, relation between extension and time for various
loads at these temperatures should be as indicated in
Fig. 200.

Two interesting and fundamental problems arise.   Do
the curves typified in Fig. 199 become truly horizontal when
the stress is reduced to some definite value—i.e., does a
" limiting creep stress " really exist—and at what tempera-
ture does strain hardening disappear in different metals ?   It
is apparent that a metal whose behaviour at some given
temperature is typified by the curves in Fig. 199 is likely
to be more useful than one possessing time-extension curves
similar to those in Fig. 200.   Hence the higher the tempera-
ture at which a metal can be strain hardened, other things
being equal, the more useful it is likely to be to the engineer.

* It may be suggested that this description is not strictly true in that work
at any temperature will presumably distort the grains of a solid metal and hence
harden them.   At temperatures above a certain minimum, however, recrystallisa-
tion occurs very quickly, removing the induced hardness.   The speed of re-
crystallisation decreases as the temperature is lowered and eventually becomes
slower than that at which the hardness is increasing under the given conditions of
strain.   When this occurs, the metal exhibits hardening effects.   It is likely that
the actual temperature at which this occurs will vary, for any particular metal,
with the rate at which it is being strained.

The first problem can only be solved within the limits of accuracy with which constancy of length can be determined.* It is not solely a question of extreme accuracy of measurement, however—it is not impossible to determine a movement of less than one part in a million on a test piece two inches long—the temperature of the test piece must be controlled within very close limits or these refinements in measurement are of no value. A rise in temperature of 1° C. will
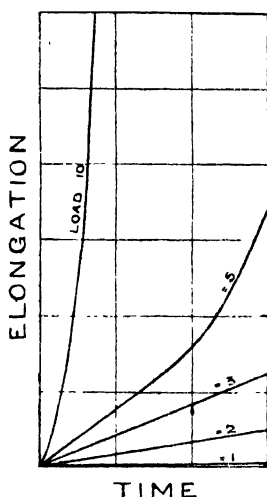
FIG. 200. Relation between elongation and time ; metal does not strain harden.

cause a test piece to elongate 14 or 15 parts per million, so that unless temperature can be controlled to considerably less than one degree, refinements in measurement below about one part in ten thousand are quite useless. It follows, therefore, that determinations of rates of flow of the order of one part in a million per hour can only be made in such cases by observing the behaviour of the test piece over a considerable time. For example, if an accuracy of measurement (including the necessary degree of temperature control) of one in ten thousand is obtainable, a duration of test of at least a hundred hours is necessary to determine whether a movement in excess of one part per million per hour is taking place.

It is probable that in few published creep stress values

* * This subject has been discussed in some detail by Dr. Hatfield ; see " The Metallurgist " (Supplement to " Engineer "), 1929, pp. 108 and 117.

has the rate of extension of the various test pieces been determined to a smaller value than one millionth of an inch per inch per hour and many determinations do not reach this degree of accuracy.   It may not be amiss therefore to mention that, at this rate of creep, a bar 12 inches long would extend 0·105 inch in a year.   Whether such an extension would be serious or not from a practical standpoint would depend on the particular purpose for which the steel was used.   Baumann* has recently discussed this subject in relation to the design of equipment for use with high temperature steam and has suggested the following maximum permissible values of the rates of creep for the parts indicated :—

(1) turbine disc pressed on shaft   1 in 10^9 per hour.

(1) bolted flanges, turbine cylinders   1 ,, 10^8 ,,

(8) steam piping, welded joints, boiler tubes 1 ,, 10^7 ,,

(4) superheater tubes ...   .   1 ,, 10^6 ,,

In the last case, the value might be increased to 1 in 10^5 per hour if the tubes were easily replaceable.   As a test piece 2 inches long elongating at the rate of 1 in 10^8 per hour would lengthen in a year only by 0·000175 inch, the difficulties of determining such rates of creep will be apparent.

The question as to whether a " limiting creep stress " in the true sense of the term really exists at high temperatures is one to which an answer is not yet forthcoming.   It may be pointed out, however, that if available data on the relationship between creep rate and stress be plotted logarithmically, a practically straight line is produced with no suggestion of a creep limit.   This was shown by R: W. Bailey† to apply to the results obtained on Armco iron at the National Physical Laboratory and, more recently, by Norton‡ on an extensive range of steels.   In Fig 201 for example, are plotted the data on Armco iron extracted by Bailey from the N.P.L. curves and they afford little evidence that, at any of the temperatures under test, the rate of creep becomes zero at some given stress.   On the other hand, they do suggest that

* " Some considerations affecting future developments of the steam cycle."
K. Baumann. " Engineering," Nov 7th, 1930, p. 597.

† " Engineer," May 3, 1929, p. 488.

‡ " The Creep of Steel at High Temperatures."   F. H. Norton. 1929.

the sensitiveness of the apparatus did not permit a rate of creep of less than 1 in $10^{5\cdot3}$ per hour to be measured.

Norton carried his measurements to an accuracy of 1 in 10^7 per hour and found no evidence of the rate of creep becoming zero. It seems probable therefore, that the engineer will have to be content with " creep stress " values
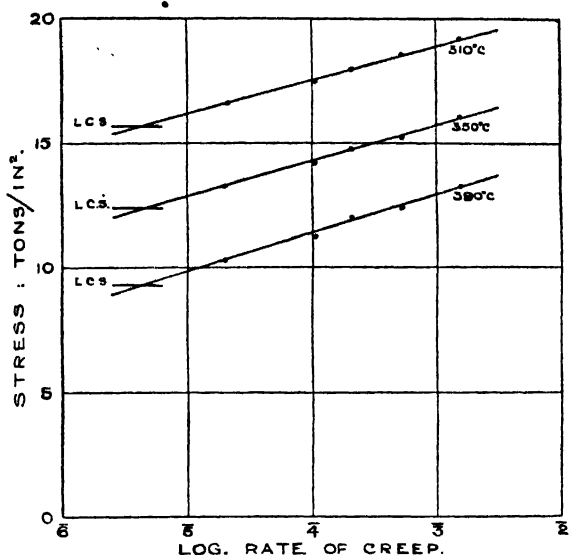
FIG. 201. Relation between stress and rate of creep of Armco iron at various temperatures. (N.P.L. data; L.C.S. = Limiting creep stress.)

which have reference to certain definite rates of creep and from which he will endeavour to estimate the useful life of his high temperature equipment. Obviously the permissible rates of creep will vary in different parts of that equipment. Equally obviously, experimenters who investigate creep stress values should state to what rate of creep their data have reference, otherwise the latter's value as a basis of design will be limited. The accumulation of such data takes time ; meanwhile the engineer has perforce to make use of such values as are extant. In connection with equipment for use with steam at high temperatures, for which the need of accurate " creep " data is urgent, it may be mentioned that there is a considerable amount of practical experience among engineers as to behaviour of mild steel at 750° F. (399° C.)

and such information may be usefully coupled up with the
available comparative data obtained by creep stress methods
on similar steel and on other types of steel at this and higher
temperatures.   Incidentally, it may be noted that if the
published data for limiting creep stress values be examined
in this light, much better agreement is found between the
results of different investigators.   For example, Fig. 202
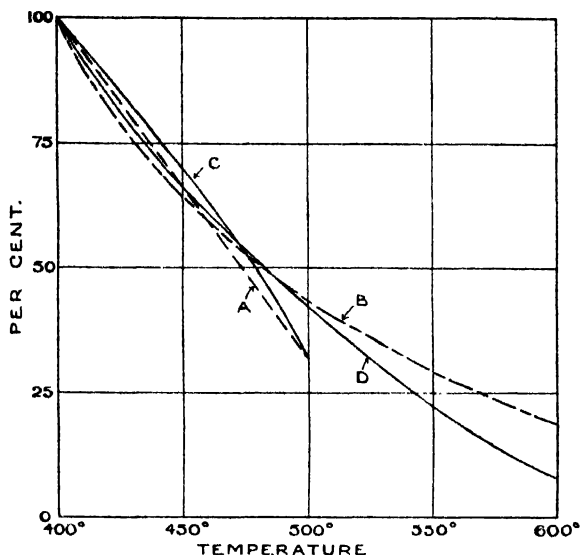
Fig. 202.   Creep stress of mild steel at 450°/600° C. as a percentage of
its value at 400° C.

Curve A.   Tapsell and Clenshaw.
    ,,   B.   Cournot and Sasawaga.
    ,,   C.   Pomp and Dahmen.
    ,,   D.   French, Cross and Petersen.

gives four sets of creep stress values obtained for mild steel
in the range 450°/600° C. plotted as percentages of the values
given by the same investigators for 400° C.   It is obvious
that these curves show much better agreement than do those,
A—D in Fig. 198, on which they are based.

Fig. 201 indicates that the maximum allowable stress
decreases fairly rapidly as the permissible rate of creep is
reduced.   Baumann* gives interesting data in this respect
with regard to mild steel (0.15 per cent. carbon) and a nickel-
chromium-molybdenum steel.   At 750° F. (399° C.) for

* *Loc. cit.*

example, he gives the relation between stress and rate of creep as indicated below :—

Material.	Stress (tons per sq. inch) producing a rate of creep per hour of 1 in.			
	10^5	10^6	10^7	10^8
Mild Steel	9·3	6·7	4·6	2·9
Ni-Cr-Mo. Steel	30·0	23·3	16·7	10·0

A similar relation was found at 800° F., 900° F. and 1,000° F. Norton* found that various high chromium and chromium-nickel steels exhibited much the same behaviour. The data in Table CXXIX are typical of his results :—

TABLE CXXIX.

Composition of Steel.				Temperature.	Stress (tons per sq. in.) producing a rate of creep per hour of 1 in		
Carbon %	Chromium %	Nickel %	Silicon %		10^5	10^6	10^7
0·43	20·16	6·99	1·35	538°C.	10·0	8·8	7·6
				649°C.	4·2	3·1	2·2
0·09	18·11	8·12	0·43	538°C.	8·9	7·6	6·7
				649°C.	3·9	3·1	2·5
0·11	13·22	0·14	0·30	538° C.	7·6	5·8	4·5
				649° C.	1·2	0·95	0·7
0·10	17·6	0·23	0·86	538° C.	4·7	3·8	3·1
				649° C.	1·2	0·95	0·7

The second problem, namely the temperature at which strain hardening effects cease to be evident, has an important bearing on the influence of time on creep stress values. It seems obvious that strain hardening effects will cease in any particular steel at the temperature at which it recrystallises completely after being cold worked. The effect on the hardness values of cold worked stainless iron induced by heating it to various temperatures has been already described ;

* *Loc. cit.*

FF

as indicated in Fig. 79, the hardness falls rapidly when the reheating temperature has exceeded ˙650° C. Most metals give similar sorts of curves, although the actual temperature producing marked softening varies considerably in different metals. Microscopical examination of the reheated specimens indicates that the marked fall in hardness corresponds to a recrystallisation of the metal, the previously distorted grains being replaced by others which are equiaxed. Samples heated to still higher temperatures are also found to be recrystallised, but the resulting grains are coarser.

Are structural changes possible at lower temperatures than those which produce the marked effect on hardness ? There is evidence that this is the case. For example, hardness curves for pure iron obtained in a similar fashion to Fig. 79 indicate that the marked fall in hardness in this metal occurs at about 570° C. Chappell* however showed that incipient recrystallisation could be detected in cold-worked iron after it had had a short reheating at 350° C. How much further would this have advanced on prolonged exposure at this temperature, and what effect would such a heating have on the hardness of a sample so treated ? If the effects of cold work are removable, even partially, by prolonged heating at temperatures below those producing the marked fall in hardness—and on the microscopic evidence mentioned above, such an effect seems within the bounds of possibility—the strain hardening of a sample produced at these temperatures by an initial extension is likely to be removed gradually and hence lead to further creep. The line of thought thus started extends far ; for example, are structural changes to be looked for in steels in general, even when not previously cold-worked, by long continued heating at temperatures of 400° or 500° C., such as are used, or are contemplated for use, in modern power plant ? Some interesting observations on this point have recently been made by R. W. Bailey† who, on examining a superheater tube which had been in use for 16,000 hours found that spheroidisation of the carbide of the pearlite had occurred near the outlet end of the tube, where the temperature had probably been about 450° C. Experiments carried out on samples cut from the inlet end of the tube (where the working temperature

* *J.I.S.I.*, 1914, I, p. 460.

† " Engineering," February 21, 1930, p. 265.

had been lower and had produced no obvious micro-structural change in the steel) showed that at temperatures between 600° and 700° C., the relationship between absolute temperature and time to produce spheroidisation followed an exponential law, and that extrapolation of the curve obtained to the ordinate representing the life of the condenser tube gave a temperature value in the range 400°/475° C.

Presuming that the spheroidisation observed in this particular tube is really the result of prolonged exposure at about 450° C. (which seems very probable), and not of an accidental and unrecorded heating to a considerably higher temperature, there seems no reason why similar spheroidisa-tion should not be produced in other steels, including alloy steels. And as the coalescence into globules of carbide—whether existing previously as the lamellae of pearlite or the fine particles of sorbite produced by hardening and temper-ing—will tend to diminish the strength of the steel in which it occurs, it may be suggested that the results of creep tests obtained in a relatively short time (e.g. in a week or two), no matter how accurately carried out, are likely to give higher values for " limiting creep stresses " than tests occupying a much longer time. Unless, of course, the samples tested possessed, owing to prior treatment, a structure unlikely to be affected appreciably by long continued heating at the temperature under test.

When determining to what extent a heated metal part may safely be stressed in service, the designer will presumably decide the maximum amount it may distort before it ceases to function properly. It will be obvious that the deter-mining factor in calculating the maximum permissible stress will depend on whether the operating temperature is such as to cause the metal to function under stress in the manner typified in Fig. 199 or in Fig. 200. In the former case, the metal may extend appreciably (presuming the stresses are in tension) when the load is applied but afterwards may possess a rate of creep of almost negligible magnitude. Hence, in many cases of this kind the allowable stress is determined by the immediate extension of the part when loaded and not by its subsequent rate of creep. On the other hand, at temperatures where the behaviour of the metal is typified by Fig. 200, rates of creep are the determining factor in deciding permissible stresses. This division of characteristics

may be summarised in the curves shown in Fig. 203. Curve ABC marks the stress below which creep does not exceed some specified low rate, e.g., one part per million per hour. At atmospheric temperature this curve approaches
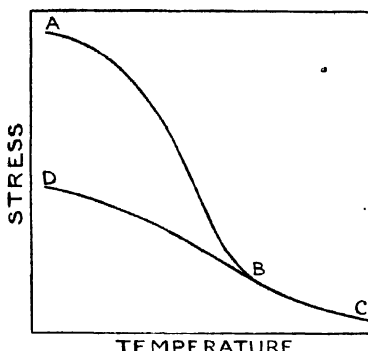
Fig. 203. Typical curves representing the behaviour of steel at high temperatures; see pages 435 and 436.

very closely the tensile strength of the metal. On the other hand, the maximum stress which may be applied without producing appreciable plastic flow is related to temperature in the manner indicated by a curve DB. At atmospheric temperature this curve marks the elastic limit of the steel. Under combinations of stress and temperature included in the area ABD, the steel will distort plastically when the stress is applied but after this, the dimensions of the part will either become constant or change at a rate less than the permitted rate of creep.

At the present time the amount of data regarding the creep rates of various types of corrosion resisting steels is somewhat meagre. The curves in Fig. 204 summarise the results obtained by French, Cross and Peterson* on mild steel, 20 per cent. chromium steel and an austenitic chromium-nickel-silicon steel. All these steels contained approximately the same amount of carbon. The broken lines on the left-hand side of the diagram mark the loads producing an initial extension of the amount indicated (0·1 or 1·0 per cent. respectively) while the full lines to the right give the relationship between rate of creep, load and temperature. The high

* " Creep in Five Steels at Different Temperatures." Bureau of Standards, Tech. Paper No. 362. January 10, 1928.

chromium steel exhibits a marked improvement on the mild steel, particularly at temperatures between 400° and 600° C.

FIG. 204. Creep rates of steels (French, Cross and Petersen).

Curve	Carbon %	Chromium %	Nickel %	Copper %
A, A¹, D, D¹	0·24			
B, B¹, E, E¹	0·28	20·5		0·98
C, C¹, F, F¹	0·24	18·1	23·3	

Curves A, B, C.	Stress producing creep rate of 1 in 10⁶ per hour.
,, D, E, F.	,, ,, ,, ,, ,, 1 ,, 10⁵ ,, ,,
,, A¹, B¹, C¹.	,, giving initial extension of 0·1 per cent.
,, D¹, E¹, F¹.	,, ,, ,, ,, ,, 1·0 ,, ,,

The austenitic steel shows to advantage above 500°C., its superiority over the chromium steel being very evident at about 600° C.

F. H. Norton* tested a considerable number of steels at temperatures between about 500°. and 800° C. Table CXXX contains his results on steels of the stainless type and also on a few others for comparison. Some of these are also plotted in Fig. 205. The advantages of the stainless irons over mild steel, and some of the ordinary constructional
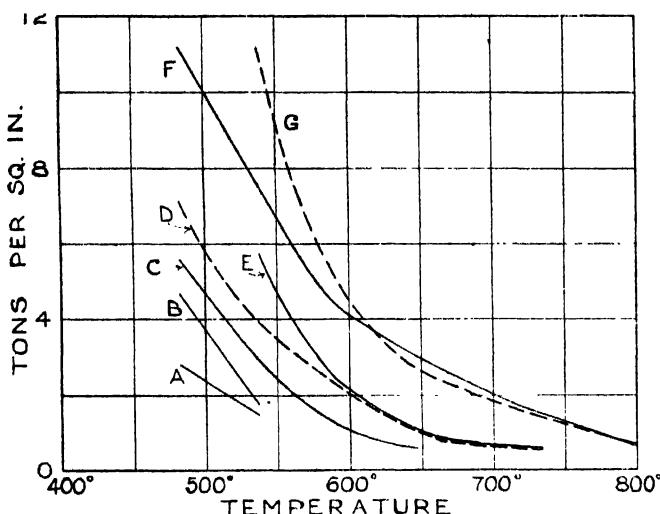
FIG. 205.   Stresses producing rates of creep of 1 in 10^6 per hour. (Norton).

Mark	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Tungsten %
A	0·8	—	—	—	—	—
B	0·20	—	—	—	—	—
C	0·34	0·17	0·46	—	—	0·74
D	0·10	0·86	0·31	17·6	—	—
E	0·11	0·30	0·45	13·22	—	—
F	0·09	0·43	0·38	18·11	8·12	—
G	0·14	1·09	0·43	6·37	19·01	—

alloy steels is again evident. It will also be noticed that an increase in chromium content from about 13 to 17 per cent. produced no beneficial effect on the strength of the material ; in fact, below about 600° C., the lower chromium iron is decidedly the stronger. Similar results were found by the author ; stainless irons containing 14·1 and 17·1 per cent. chromium were found to creep at a rate of 6 millionths of an inch per inch per hour under a load of 2½ tons per square inch at 600° C. but, under the same condition, a third iron

* "The Creep of Steel at High 'Iemperatures." F. H. Norton. McGraw-Hill Pub. Co., 1929.

TABLE CXXX.

Stresses (tons per sq. in.) Producing Creep Rates of 1 in 10⁸ per hour (Col. A) and 1 in 10⁷ per hour (Col. B).

(F. H. Norton.)

Mark.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Tungsten %	Vanadium %
A	0·20	—	—	—	—	—	—
B	0·45	0·20	0·42	—	—	—	—
C	0·84	0·19	0·57	—---	3·46	·—	—-
D	0·40	0·20	0·59	0·66	1·30	—	—
E	0·40	0·25	0·62	0·79	--	—	0·57
F	0·11	0·30	0·45	13·22	—	—	—
G	0·10	0·86	0·31	17·6	—	—	--
H	0·09	0·47	0·47	12·4	—	—	—
J	0·29	0·36	0·80	26·94	—	—	—
K	0·14	0·32	0·45	18·15	8·23	—	0·13
L	0·14	1·09	0·43	6·37	19·01	—	0·18
M	0·12	0·76	0·53	24·90	19·67	—	0·18
N	0·43	1·35	0·52	20·16	6·99	0·60	0·23
O	0·09	0·43	0·38	18·11	8·12	--	—

Mark.	482° C.		538° C.		593° C.		648° C.		734° C.		815° C.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
A	4·69	3·48	1·74	1·43	—	—	—	—	—	—	—	—
B	5·14	3·93	2·01	1·43	0·94	0·67	0·40	0·25	—	—	—	—
C	—	—	2·23	1·56	0·76	0·54	—	—	—	—	—	—
D	5·80	4·69	2·68	2·01	0·98	0·71	0·33	0·25	—	—	—	—
E	—	—	2·68	2·23	1·02	0·76	0·49	0·31	—	—	—	—
F	—	—	5·8	4·45	2·36	1·78	0·94	0·71	·—	—	—	—
G	7·14	5·35	3·8	3·12	2·36	2·01	0·94	0·71	0·54	0·40	—	—
H	—	—·	—	—	2·23	1·65	1·16	0·67	0·62	0·40	—	—
J	—	—	—	—	—	—	0·71	0·45	0·18	0·08	—	—
K	—	—	—	—	—	—	4·02	2·90	—	—	—	—
L	—	—	11·15	8·93	4·91	4·24	2·68	2·46	1·43	1·25	0·49	0·33
M	—	—	—	—	—	—	3·35	2·46	—	—	—	★
N	—	—	8·48	7·59	—	—	3·12	2·23	—	—	—	—
O	11·15	9·15	7·59	6·70	4·24	3·57	3·12	2·46	—	—	0·38	0·33

containing 20·5 per cent. chromium, extended about ten times as fast.

Norton's results also demonstrate the superior strength
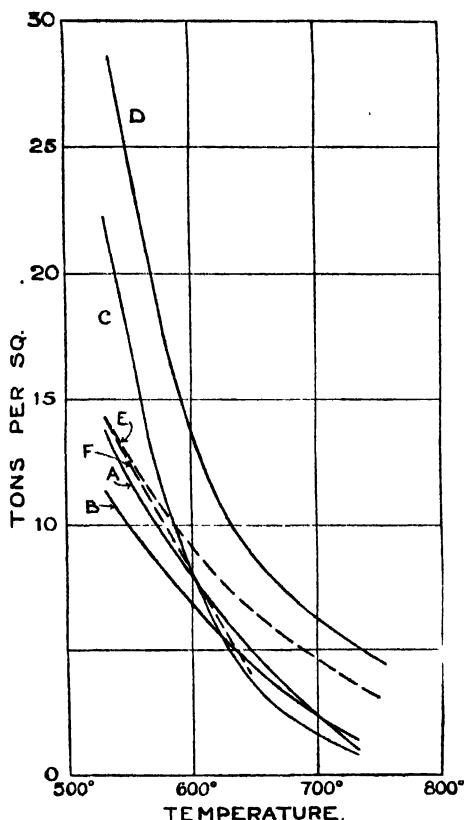
FIG. 206. Stresses producing rates of creep of 1 in 10⁸ per hour. (Bureau of Standards.)

Mark	Carbon %	Solicon %	Man-ganese %	Chromium %	Nickel %	Tung-sten %	Treatment
A	0·32	0·03	1·52	13·93	34·9	—	As rolled
B	0·28	0·03	1·45	11·12	35·9	0·34	Annealed 900° C
C	0·28	0·07	1·50	10·64	38·6	1·77	As rolled
D	0·29	1·18	0·50	19·86	8·0	4·5	As forged
E	0·15	0·22	0·35	17·32	8·46	—	As rolled
F	0·15	0·22	0·35	17·32	8·46	—	W.Q. 1,000° C.

of the austenitic steels, as compared with the stainless irons, at temperatures above about 500° C.

More recently, the results of an extensive investigation

at the Bureau of Standards* into the properties of iron-nickel-chromium alloys has become available. A large number of alloys were tested as regards their flow characteristics ; the data relating to those coming within the scope of this book are given in Figs. 206 and 207. Perhaps the
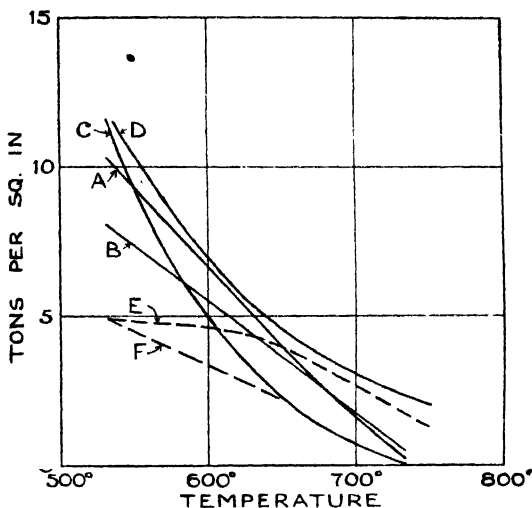
Fig. 207. Stresses producing rates of creep of 1 in 10⁶ per hour. (Bureau of Standards.)

Analyses as in Fig. 206.

most remarkable feature of these results is the poor behaviour, above about 600° C., of the high nickel steel containing 1·77 per cent. tungsten (steel C). Apart from this steel, the data given indicates that the addition of tungsten has a distinct strengthening effect at high temperatures, steel D, for example, being outstandingly good. The relative behaviour of samples E and F is interesting. The former was in the rolled condition and microscopic examination showed that its structure was considerably coarser than that of the second bar (F) which, incidentally, had been softened at 1,000° C. after rolling. Evidence has been obtained by other investigators† that under certain circumstances an alloy in a coarsely grained condition may be distinctly stronger at high temperatures than when possessing a very

* " Flow Characteristics of Special Fe-Ni-Cr Alloys and Some Steels at Elevated Temperatures." Research Paper No. 192. July, 1930.

. † " Some Alloys for Use at High Temperatures." Rosenhain and others. *J.I.S.I.*, 1930, I, p. 225.

fine structure and the results given above would appear to confirm this. At the same time they suggest that different batches of material of similar analysis may exhibit considerable variations in their behaviour at high temperatures.

A very comprehensive report on nickel-chromium and complex iron-nickel chromium alloys has been issued by the National Physical Laboratory.* The work was mainly concerned with the higher nickel-chromium alloys and it showed that it was possible to produce complex types of these alloys possessing remarkable resistance to deformation when hot. In particular the authors refer to an alloy containing 30 per cent. chromium, 30 per cent. nickel, 33·5 per cent. iron, 4 per cent. tungsten, 1·5 per cent. carbon and 1·0 per cent. silicon which had a life of 50 days under a load of six tons per square inch at 800° C. Alloys so hard as this are almost incapable of being forged and hence are used as castings. This, however, is no detriment as regards their strength at high temperatures because tests on alloys of a somewhat softer type, which could be forged or rolled, showed that these were invariably less strong at 800° C. after being worked than in the cast condition. The reason for this is not yet understood.

A reference to Figs. 206 and 207 shows that a chromium-nickel steel of the " 18/8 " type containing, in addition, 4·5 per cent. tungsten, has remarkably good properties. Tapsell and Remfry† tested a steel containing :—

Carbon	...	...	...	0·46%
Silicon ...	...	...	..	1·20%
Manganese	...	...	..	1·09%
Chromium	...	...	..	14·0%
Nickel ...	...	...	..	26·5%
Tungsten	...	...	..	3·59%

and obtained the following creep stress values :—

Temperature.	Estimated Limiting Creep Stress.
600° C.	... 11 tons per sq. inch.
700° C.	... 6 ,, ,, ,,
800° C.	... 2 ,, ,, ,,

It is probable that these figures have reference to a rate of creep of about 1 in 200,000 per hour ; hence they are more

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* "Some Alloys for Use at High Temperature." Rosenhain and others. *J.I.S.I.*, 1930, I, p. 225.

† Engineering Research Board, Special Report No. 15, 1929.

Plate XLV

Fig. 208. Intergranular cracks in steel containing 0·18 per cent. carbon, 16·5 per cent. chromium, 10·8 per cent. nickel after 3 weeks' test at 700° C. under load of 2 tons per sq. in. × 100.

To face page 443.]

comparable with the results in Fig. 206 or in the upper part of Fig. 204 than with those in the lower part of the latter diagram or in Fig. 207.

From an examination of the data given in the last few pages, it would appear that :—

(1) Stainless irons containing 12/14 per cent. chromium are distinctly stronger than mild steel, particularly in the range 400°/600° C. Raising the chromium content to 17/20 per cent. lowers the strength.

(2) The austenitic chromium-nickel steels, containing 15/20 per cent. chromium and 12/8 per cent. nickel are distinctly stronger than the stainless irons at temperatures of about 450° C. and over. Still greater strength at these high temperatures may be obtained by the addition of tungsten or silicon, particularly the former. The value of an increase in nickel content to 25/35 per cent. is not definitely established from these results.*

The austenitic steels have however a rather disturbing feature which reduces their value in certain ranges of temperature. It has already been shown that carbide is precipitated along the grain boundaries of the austenite when such steels are heated in the range 500°/900° C. Owing to this precipitation, the steels are liable to develop intergranular cracks if they are stressed continuously in tension while heated in this temperature range. For example, a test piece of steel containing 0·18 per cent. carbon, 16·5 per cent. chromium and 10·8 per cent. nickel fractured suddenly after being loaded for three weeks at 700° C. with 2 tons per square inch. Prior to the fracture occurring, the test piece (2 in. gauge length) had extended less than 0·001 in. The fracture was entirely intergranular and microscopical examination showed that numerous intergranular cracks had been formed in the material adjacent to the fracture. Some of these are shown in Fig. 208. Tapsell and Remfry† found that steel containing 0·46 per cent. carbon, 14·0 per cent. chromium, 26·5 per cent. nickel and 3·59 per cent. tungsten developed similar cracks at 700° and 800° C. during the

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* Experience in the hot working of chromium-nickel steels of different nickel contents indicates very strongly, however, that the higher nickel alloys (e.g., those containing 20 per cent. or more) are much harder to deform at temperatures above 800°/900° C.

† *Loc. cit.*

course of creep-stress determinations.   Specimens at 800° C. fractured in 78 and 152 days after extending not more than 2 per cent. of their length.   Similar results were also found by French and his collaborators at the Bureau of Standards ; thus the chromium nickel steels of the " 18/8 " type which they tested (steels E and F, Figs. 296 and 207) developed marked intercrystalline cracks at temperatures between 625° and 750° C. and to a less extent at 530° C.   They state that when the specimens were allowed to remain under load until fracture occurred, the fracture was intercrystalline and grain separation was observed at some distance from the fracture.   Similar intercrystalline weakness was noted in steel D at 630° and 750° C. and in steel C at 650° C. (Figs. 206 and 207.)

It is obvious that this type of intercrystalline weakness exists in austenitic steels possessing widely different compositions.   Meanwhile, until further evidence is available as to whether intergranular fracture may occur under any load in this temperature range, or is only likely to be produced if the stress exceeds certain minima at given temperatures, it would appear undesirable to use these steels under conditions where their failure in this manner would be liable to have serious consequences.

An inspection of the various curves connecting creep stress values with temperature brings out one fact very strongly.   The safe stress for any particluar steel falls so rapidly with rise in temperature that an increase of 10° C. frequently lowers this stress about 10 per cent.   It is thus obvious that either a considerable factor of safety must be used to cover possible or probable temperature fluctuations in service—in which case the prescribed working stress will frequently be very low—or it must be arranged with certainty that all temperature fluctuations shall be below, and not above, that selected for determining the creep stress value to be used as a basis for design.

The time-consuming character of creep tests has led to attempts to devise some modified form of test which could be carried out in a few days and yet give results which could be used as a basis for design.   Prof. Galibourg,* for example, tested a number of steels in connection with the recent

* " Essais de Traction à Chaud sur Aciers."   Centre d'Information du Nickel. Paris, 1929.

extension of the power station at Issy-les-Moulineaux. The behaviour of the steels at 450° C. was in question and the test consisted in determining with an accuracy of measurement of 1 in 70,000, whether or not creep was produced under a given load in 12 hours. No steels of the stainless type were included in the tests but the results on a mild steel (0·22 per cent. carbon) indicated that creep was produced in this material at 6·5 tons per square inch but not at 4·3. These results may be compared with the data given in Fig. 198.

Dr Hatfield* has advocated a rather more elaborate form of test, giving a value which he has termed " time-yield." In this test, the test piece is allowed 24 hours under load to permit any initial movement to be completed and then the presence or absence of creep determined over a further period of 48 hours. The maximum initial extension is arbitrarily fixed at 0·5 per cent. of the gauge length and an accuracy of measurement during the " creep " period of the order of one part per million per hour is postulated. Dr. Hatfield considers that a value of two-thirds of the " time-yield " may be used by designers as a safe stress in tension. His results are quoted in full in Table CXXXI and the values given there may be compared with the " creep-test " results previously recorded.

If the conditions for Dr. Hatfield's " time-yield " be examined, it will be seen that they depend on at least two circumstances : (a) an initial extension limited to 0·5 per cent., and (b) a subsequent rate of creep not greater than 1 in 10^6 per hour. Which of these two will be the deciding factor in determining the value of the " time-yield " will depend, for any one steel, on the temperature of test ; that is, on whether the temperature is such as to cause the steel to behave in the manner typified by Fig. 199 or by Fig. 200. At certain temperatures, at least, the deciding factor will not be the same for different steels. Possibly one of the most interesting features of Dr. Hatfield's results is the poor behaviour of steel J, containing roughly 18 per cent. chromium and 8 per cent. nickel. On material of similar analysis, Norton† obtained values of approximately 10 tons per

* " Permanence of Dimensions under Stress at Elevated Temperatures." *J.I.S.I.* 1930., II, p. 215.

† *Loc. cit.* See Fig. 205.

TABLE CXXXI.

Values for " Time Yield " of various steels.   (Dr. Hatfield.)

Mark.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Molybdenum %	Tungsten %	Vanadium %	Aluminium %	Cobalt %
A	0·25	0·11	0·58	—	0·18	—	—	—	—	—
B	0·88	0·21	0·58	—	0·20	—	—	—	—	—
C	0·24	0·20	0·55	nil	3·8	—	—	—	—	—
D	0·25	0·28	0·63	1·35	3·10	0·55	—	0·22	—	—
E	0·46	0·27	0·59	1·72	0·07	0·33	—	—	1·01	—
F	0·51	3·16	0·88	8·26	0·16	—	—	—	—	—
G	0·15	0·81	0·36	14·66	0·19	—	—	—	—	—
H	0·29	0·80	0·28	13·04	0·35	—	—	—	—	—
J	0·16	0·29	0·30	17·82	8·04	—	—	—	—	—
K	0·51	0·40	0·63	12·64	9·81	—	3·75	—	—	—
L	1·70	0·51	0·34	12·45	—	0·86	—	0·87	—	—
M	0·35	0·23	0·21	3·37	—	—	10·14	0·43	—	—
N	0·67	0·87	0·32	3·96	—	—	16·14	0·60	—	—
O	0·74	0·42	0·23	3·82	—	—	18·06	1·18	—	4·15

Mark	Treatment.	Tensile str'ngth at 15°C.	" Time Yield " : tons per sq. inch.						
			200°C.	300°C.	400°C.	500°C.	550°C.	600°C.	700°C.
A	A.C. 800°/900° C.	33·9	—	13·5	8·1	4·2	2·3	—	
A	Annealed 660° C. for 48 hrs.	29·8	—	—	6·3	3·5	1·68	—	—
B	A.C. 850° C.	38·2	—	—	8·1	4·5	2·5	—	—
C	A.C. 850° C.	40·85	—	—	10·2	4·7	2·1	—	—
D	O.H. 850°C., T.650°C. ...	60·0	—	—	18·0	7·5	2·9	—	—
E	" "	67·6	—	—	16·5	5·5	2·3	—	—
F	O.H. 950°C., T.750°C. ...	60·2	—	—	19·0	2·5	—	—	—
G	A.H. 1000°C., T.700°C. ...	45·1	—	—	14·75	6·0	—	—	—
H	O.H. 975° C., T.750° C. ...	48·0	—	25·0	14·5	5·75	—	—	—
J	Softened 1150° C. ...	44·1	10·0	7·75	6·75	6·2	—	—	—
K	„ 1050° C. ...	56·2	—	—	19·5	12·6	7·5	4·2	2·0
L	A.C. 1000° C., T.650°C. ...	70·3	—	—	—	7·75	3·5	0·6	—
M	O.H. 1150° C., T.650° C.	89·2	—	—:	52	20·0	13·0	1·0	—
N	Annealed 900° C. ...	60·5	—	—	—	5·25	3·0	1·0	0·5
N	Hardened 1320° C., T. 590° C., 3 hours	—	—	—	—	21·0	—	1·0	—
O	Annealed 900° C. ...	57·7	—	—	—	6·25	4·0	2·3	—
O	Hardened 1320° C., T. 600° C., 3 hours	—	—	—	—	22·0	—	3·0	—

square inch at 500° C., 6·5 at 550° C., 4·0 at 600° C., and 2·0 at 700° C. for the stresses producing a rate of creep of 1 in 10^6 per hour ; values roughly twice as great as those of Dr. Hatfield for the same rate of creep.   The cause of this

difference may possibly be sought in the very short duration of the " time-yield " test ; in the author's experience in tests at 500°/700° C., a distinctly longer period than 24 hours has frequently elapsed before a test piece has reached a reasonably constant rate of creep.   If the measurements as regards creep be taken before the period of " initial extension " is over, the estimated stress values for given rates of creep are likely to be lower than if this initial movement of the test piece had been completed.

Even tests of the nature of Dr. Hatfield's " time-yield " occupy a considerable time and when a series of alloys are to be surveyed in order that those likely to be of the greatest service under given conditions may be selected, some quicker method of test is desirable.   The author believes that tensile tests carried out under strictly comparable conditions will afford useful information in this respect and a similar opinion has been expressed by Dr. Rosenhain, Dr. Hatfield and Mr. Brearley, among others.   If tensile tests, pulled at the same rate at some given temperature, on two different alloys show that one has a tensile strength 50 or 100 per cent. greater than the other, it is logical to assume that the former is likely to sustain indefinitely a greater load than the latter at the same temperature.   For example, the data given in Table CXXXII* suggests that the 14 per cent. chromium steel will be stronger than mild steel at temperatures between 500° and 700° C. but that the complex chromium-nickel-tungsten steel will be markedly superior to either at the same or higher temperatures.   The silicon-chrome valve steel is likely to have good strength up to about 600° C., but its value will diminish rapidly above this temperature.

Results obtained by Henshaw† on typical valve steels are given in Table CXXXIII.   Again the austenitic chromium-nickel-tungsten steel is superior to the others but one may also note the much higher values given by the chromium-silicon steel C, as compared with steel D, low in silicon but otherwise similar in analysis to C.   As regards the cobalt-chromium steel E, the results hardly suggest that this steel has a value commensurate with its cost as compared, for instance, with steel C.   The nickel-chromium steel A and the

* Taken from " Heat Resisting Steels." Pt. II. " Mechanical Properties." Dr. W. H. Hatfield.   J.I.S.I.   1928, I, p. 573.

† " Valve Steels."   P. B. Henshaw.   J. R. Aero. Soc.   March, 1927.

Table CXXXII.

Tensile Tests at High Temperatures (Hatfield).

Mark.	Carbon	Silicon	Manganese %	Chromium %	Nickel %	Tungsten %	Treatment.
A	0·32	0·19	0·53		0·09		A.C. 900° C.
B	0·29	0·27	0·60	0·89	3·41		O.H. 830° C., O.Q. 600° C.
C	0·27	0·26	0·30	13·30	0·42		O.H. 950° C., T. 760° C.
D	0·60	3·98	0·52	8·75	0·23		O.H. 1075° C., T. 900° C.
E	0·40	0·97	0·41	13·65	10·31	3·53	A.C. 950°C.

Temperature, °C	A.		B.		C.		D.		E.	
	Y.P.	M.S.	Y.P.	M.S.	Y.P.	M.S.	Y.P.	M.S.	Y.P.	M.S.
15	22·2	36·6	48·8	57·8	35·7	48·5	59·0	68·0	36·0	63·0
100	18·8	33·7	47·5	56·4	35·8	45·9	58·5	68·5	37·5	53·5
200	20·7	40·7	45·6	54·85	35·4	43·5	50·2	63·0	35·3	49·4
300	19·4	43·55	48·5	55·28	33·9	41·3	45·9	58·2	32·6	43·4
400	19·4	40·7	46·9	55·41	31·2	37·8	45·0	57·0	29·4	42·7
500	15·0	28·6	39·0	44·91	—	32·7	39·0	45·3	26·0	39·5
600	—	15·5	—	23·62	—	18·8	—	24·5	—	34·1
700	—	8·07	—	12·31	—	12·1	—	10·08	—	28·2
800	—	5·47	—	5·6	—	5·04	—	4·87	—	17·2
900	—	3·75	—	4·53	—	—	—	2·82	—	12·0
1000	—	2·65	—	2·97	—	—	—	—	—	6·02

Table CXXXIII.

Tensile Tests at High Temperatures (Henshaw).

Mark	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Vanadium %	Tungsten %	Cobalt %	Molybdenum %	Treatment.
A	0·43	0·25	0·45	0·75	2·8	—	—	—	—	O.H. 780°C., O.Q. 625°C.
B	0·40	0·89	0·44	13·0	—	—	—	—	—	O.H. 950°C., A.C. 700°C.
C	0·54	2·5	0·69	8·2	—	—	1·96	—	—	A.C. 1000°C., A.C. 800°C.
D	0·61	0·34	0·40	9·56	—	—	—	—	—	A.C. 950°C., A.C. 700°C.
E	1·50	0·42	0·27	13·25	—	—	—	3·7	0·72	A.C. 950°C., A.C. 750°C.
F	0·73	0·16	0·18	3·75	—	0·5	18·9	—	—	A.C. 950°C., A.C. 800°C.
G	0·45	1·75	0·65	12·67	12·81	—	2·1	—	—	A.C. 800°C.

	MAXIMUM STRESS (TONS PER SQUARE INCH)								
Mark.	15° C.	600° C.	650° C.	700° C.	750°C.	800° C.	850° C.	900° C.	950° C.
A	56·5	34·0	23·6	13·5	11·2	9·2	6·9	4·5	—
B	48·3	24·2	17·3	10·2	8·0	6·1	5·6	7·9	—
C	63·0	42·0	34·5	25·3	17·8	10·7	7·2	3·9	3·0
D	54·0	36·5	30·0	19·0	13·0	7·0	7·2	7·3	5·2
E	58·0	45·0	30·5	24·8	13·6	10·0	5·8	8·1	6·0
F	61·0	41·0	26·6	21·3	16·8	9·8	7·7	8·5	5·6
G	68·0	42·6	38·3	33·8	28·6	24·0	19·4	15·0	12·5

high speed steel F have been included for comparison as both these types of steel have been widely used for valves.

Apart from this, the tensile test affords useful information, with regard to the relative behaviour of metals when subjected to stress for short periods at high temperatures. Thus, Henshaw has urged its value as a guide to the selection of steels for valves for internal combustion engines. Similar considerations obviously apply in connection with the relative ease or otherwise of hot working different steels; the property it is desirable to measure in this case is resistance
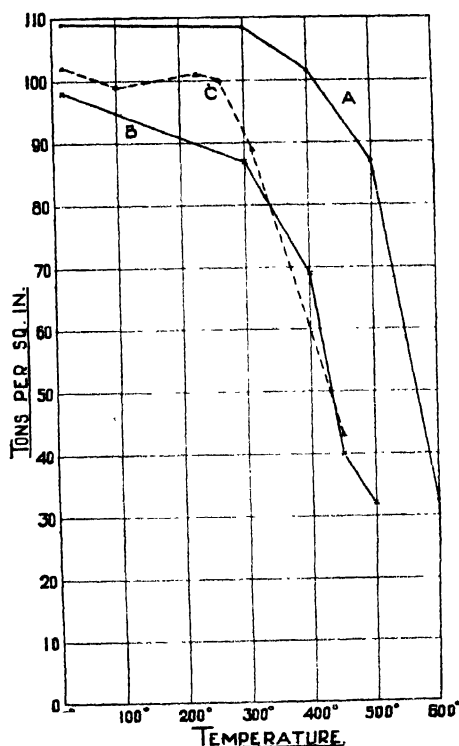
FIG. 209. Tensile strength of hardened steels at temperatures up to 600°C. :—

Curve A. Stainless Steel.
,, B. Ordinary Steel, 1·0 per cent. carbon.
,, C. ,, ,, 0·5 per cent. carbon.

to rapid flow under impact or quickly applied pressure and it seems obvious that properly conducted tensile tests will
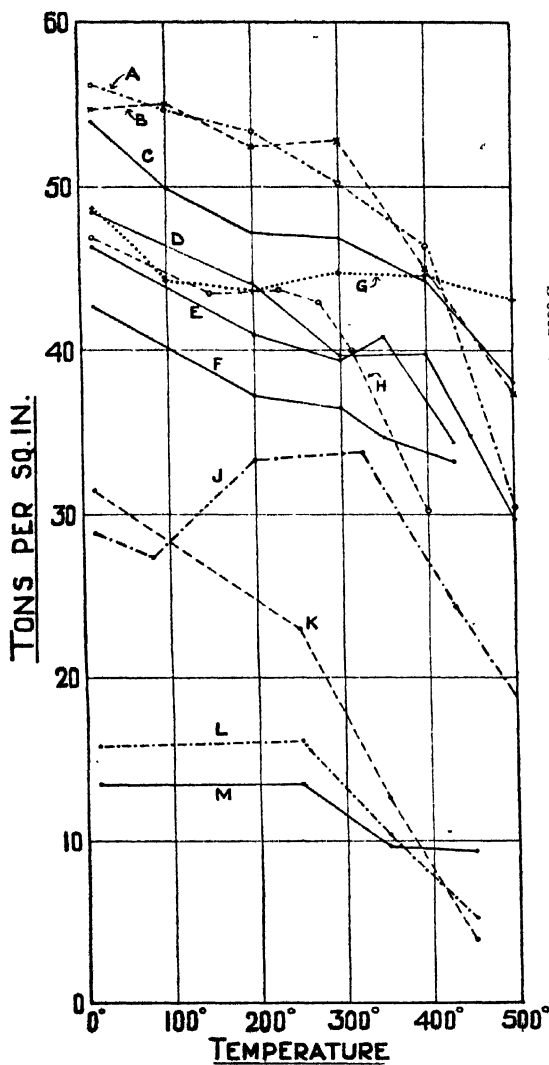
Fig. 210. Tensile strength of various engineering materials at temperatures up to 500° C. :—

A. Nickel Chrome Steel (*Author*).
B. High Speed Steel (*Dickenson*).
C. Stainless Steel (*Dickenson*).
D.   „   „   (*Author*).
E.   „   „   („   „).
F. Stainless Iron („   „).

G. Nickel Chromium Alloy (65%, Nickel, 12% Chromium) (*Dickenson*).
H. Monel Metal (*Aitchison*).
J. Mild Steel (*Le Chatelier*).
K. Muntz Metal (*Aitchison*).
L. Gun Metal (*Aitchison*).

M. Phosphor Bronze (*Aitchison*).

afford evidence as to the relative " stiffness " of steels of high temperatures.

In the range of ordinary steam temperatures, e.g., up to 300°/350° C., the tensile test supplies valuable data to the engineer as regards the relative strength and hardness of the various metals he uses for steam equipment. Useful deductions may be drawn from the curves in Figs. 209 and 210. Those in the former indicate that hardened samples of the 12/14 per cent. chromium steel retain their hardness to a higher temperature than ordinary carbon steels similarly heat treated, and hence are likely to be much less eroded than the latter by superheated steam. The influence of temperatures up to 500° C. on the tensile strength of various steels and non-ferrous alloys is shown in Fig. 210 and it is evident that the 12/14 per cent. chromium steels retain their strength at these ordinary steam temperatures in a way which compares very favourably with any of the other metals.

The effects of high temperatures on the toughness of steels are also important in engineering work. It is well known that ordinary carbon steels are subject to what is known as " blue brittleness " at temperatures rather less than those showing a faint colour of heat, roughly between 300° and 500° C. The best means of measuring this brittleness is the notched-bar impact test. In carrying out this test it is almost impossible to have a furnace round the test piece while it is being broken ; however, if the test piece be heated to the required temperature, transferred rapidly to the testing machine and immediately broken, the loss of temperature occurring between drawing from the furnace and breaking is very small so that the temperature of the test piece at the moment of breaking may be regarded as being the same as that of the furnace without appreciable error. In the experiments described in the following paragraphs, the test pieces were 10 mm. square and were notched with the standard " Vee " notch, as specified in the Izod test ; they were broken, however, in a Charpy machine because the test piece may be more rapidly placed in position and broken in this machine than in the Izod.

Tests on ordinary carbon steels show that the range of " blue brittleness " is well indicated by the notched bar test. This may be seen from the curves in Fig. 211. Fig 212 shows that a similar brittle range occurs in several of the

structural alloy steels in common use.   It will be noticed, in all these curves, that the impact value rises sharply to a maximum at about 700°C. and then falls gradually.   At temperatures below that at which the maximum impact value is obtained, the test pieces break under the test ; at this
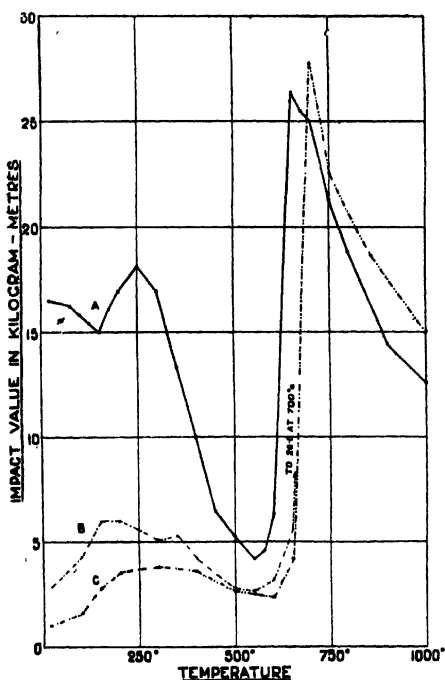
FIG. 211.   Impact values of ordinary steels at high temperatures :—

A.   0·23 % carbon.
B.   0·47 %   ,,
C.   0·73 %   ,,

temperature and above they no longer break but bend, and the gradually falling impact value in the range 700°/1,000° C. is due to the material becoming softer with increasing temperature and, therefore, requiring a smaller expenditure of energy to bend it.

In the case of the stainless irons and hardenable stainless steels, the relationship between toughness and temperature

is quite different. As may be seen from the curves in Fig. 213, the impact value of these steels is much less affected by temperature ; these materials have no range of "blue brittleness" such as is observable in Figs. 211 and 212.
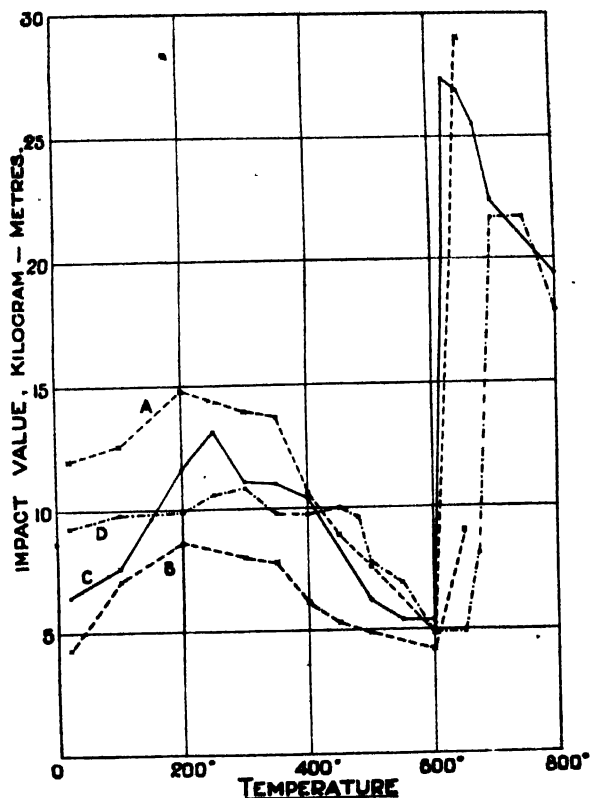
FIG. 212. Impact values of various structural alloy steels at high temperatures :—

Curve	Steel	Carbon %	Nickel %	Chromium %	Previous Treatment
A	3 % Nickel	0·32	3·34	0·02	O.H. 830° W.Q. 650° C.
B	3 % Nickel	0·32	3·34	0·02	A.H. 830° C.
C	̶ /̶ ̶̶̶̶	0·36	4·87	—	O.H. 830° WQ. 625° C.
D	Nickel Chrome	0·31	3·50	1·58	A.H. 830° WQ. 650° C.

Results obtained from two austenitic steels, of high and low carbon contents, are plotted in Fig. 214. The lower carbon steel exhibits a distinct minimum in the curve at 600°/650° C. At the same time, it should be emphasised

that, even at this temperature, the steel is not brittle ; an
impact value of 15 kilogram-metres indicates a very tough

FIG. 213. Impact values of stainless steels at high temperatures :

Curve	Carbon %	Chromium %
A	0·10	13·6
B	0·15	13·0
C	0·21	13·5
D	0·34	11·2

steel, as will be obvious on referring to the three previous
diagrams.   The test pieces tested at 700° C. and over did
not break and the gradual drop in impact value at higher
temperature is due to the progressive softening of the steel.
The impact value of the higher carbon steel commenced to
fall at a lower temperature than in the other, but otherwise
the curves for the two steels exhibit similar characteristics.

Henshaw* obtained the values given in Fig. 215 on a
series of valve steels.   In this case, the test pieces were
broken in an Izod machine, a special gripping device being
used which enabled the test pieces to be very quickly gripped
and broken.   The most noticeable feature here concerns the
silico-chrome steel which exhibits a very great increase in
toughness with rise in temperature.   The values obtained

* *Loc. cit.*

from the austenitic steel are lower in the range 400°/800° C. than at higher or lower temperatures; the curve for this steel is very similar to that of the higher carbon steel in Fig. 214, although the latter steel is much the tougher of the two.*

One other effect of prolonged exposure at high steam temperatures on the properties of steels requires attention.

FIG. 214.   Impact values of austenitic steels at high temperatures :-

Curve	Carbon %	Chromium	Nickel %
A	0·09	15·4	10·5
B	0·26	15·5	10·6

These temperatures of 400°/450° C.—and possibly still higher in the not distant future—are in the range of temperature which induces temper brittleness in many high tensile alloy steels.

Such steels may be heat treated to possess a tensile strength of 60 tons per square inch together with good

* 10 kgm. in Fig. 214 corresponds approximately to 72 ft. lbs. in Fig. 215.

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B	0·15	13·0
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* 10 kgm. in Fig. 214 corresponds approximately to 72 ft. lbs. in Fig. 215.

ductility and toughness, properties eminently desirable for example in certain types of bolts for use in plant dealing with highly superheated steam. But if exposure at 400°/450° C. is likely to reduce the impact value of the steel from 40/50 ft. lbs. to a tenth of this value in the course of a few days, or maybe weeks, the steel is much less valuable. Many alloy
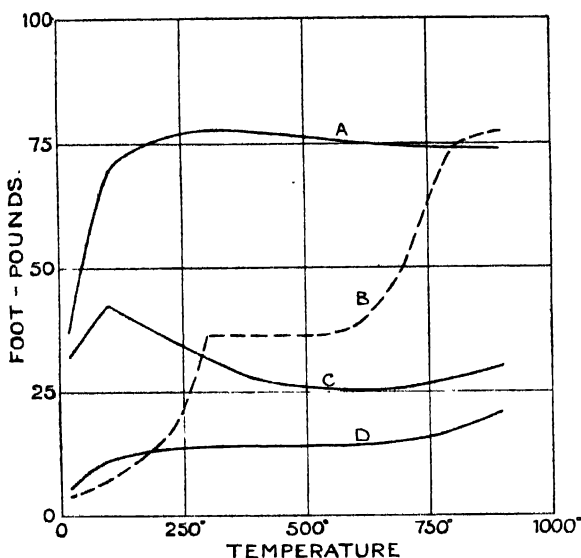
FIG. 215. Impact values of valve steels at high temperatures. (Henshaw.)

Curve	Carbon %	Silicon %	Chromium %	Nickel %	Tungsten %	Cobalt %	Molybdenum %
A	0·61	0·34	9·58				
B	0·54	2·5	8·2		1·96		
C	0·45	1·75	12·67	12·81	2·1		
D	1·50	0·42	13·25			3·7	0·72

steels, for example, the ordinary nickel, nickel-chromium and chrome-vanadium steels used so largely in engineering work, are affected in this way, and it has been reported that even certain types of nickel-chrome-molybdenum steels, which appear from tests lasting a few hours to be free from temper brittleness, have been found to have their toughness greatly reduced by several months' exposure at 400°/450° C. Little data have been published regarding the behaviour of stainless steels in this respect but the following results suggest that the 12/14 per cent. chromium steels have desirable properties.

Hardened and tempered bars of such steels were held at 400°/450° C. for 71 days; tests before and after this treatment are given below:—

Carbon %	Chromium %	Nickel	As Heat Treated.			After 71 days at 400°/450° C.			
			Brinell Hardness No.	Izod Impact Value. Ft. Lbs.			Brinell Hardness No.	Izod Impact Value. Ft. Lbs.	
0·10	13·9	0·24	149	107, 112, 112			149	103, 114, 102	
0·31	13·7	0·75	217	62, 69, 65			207	64, 71, 58	

MANUFACTURE, WORKING AND TREATMENT OF STAINLESS STEEL

CHAPTER VIII

MANUFACTURE, WORKING AND TREATMENT OF
STAINLESS STEEL

It is not intended to describe in detail the actual manufacture of stainless steels, i.e., the melting operation, slag, conditions and such like details. These matters are not of direct interest to the user of the steels and are therefore unnecessary in a book intended mainly to guide him in the selection of the most suitable types of the steel for different purposes, to indicate the best manner of working or heat treating the steel when he has received it and to describe the properties, both chemical and physical, which he may expect to obtain from it. It may be of interest, however, if a brief outline be given of the salient features of the manufacture of the steel; probably this will also help the user to understand certain peculiarities it possesses and also, incidentally, why its cost is relatively high.

The high cost of all types of stainless steel, as compared with ordinary carbon steels, is due very largely to the expense of producing suitable kinds of ferrochrome. The source of the chromium used in making the steel is the mineral chromite which consists largely of a mixture of the oxides of chromium and iron and may contain, after suitable calcination to drive off volatile matter, about 50 per cent. of the former oxide and 16 per cent. of the latter, the balance consisting mainly of magnesia, silica and alumina. As this ore occurs fairly abundantly and is not very expensive, it may occasion some surprise that the alloy made from it should be so costly, especially in view of the fact that the ore may be reduced quite easily by means of carbon, a very cheap reducing agent. Ferrochrome alloys can indeed be produced quite cheaply by this means but they are of no use for the manufacture of stainless steels owing to their very high carbon content, generally 6/10 per cent., although they are quite suitable for making many kinds of alloy steels containing only small amounts of chromium.

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Two methods are available for producing the low carbon, high chromium alloy necessary for making stainless steel, namely :—

(a) eliminating the carbon from the high carbon alloy already available ; or

(b) producing carbonless alloy at the outset by using some other reducing agent than carbon.

As regards the first alternative, it is possible, by fusing the high carbon alloy in an electric furnace with suitable slags, consisting mainly of chromium oxide and a flux, to reduce the carbon content to below 1 per cent., while other methods, e.g., Bessemerising,* allow a figure of 0·1 per cent. to be reached.   But all these processes either consume a considerable amount of electric power or are wasteful of chromium or both and hence they increase considerably the cost of the original alloy.

At least two other reducing agents are available, aluminium and silicon ; both, however, are considerably more expensive than carbon ; hence the alloys produced by their use cost much more than the high carbon product.   During the last few years, however, the cost of producing the low carbon alloy, by one means or another, has been much reduced and it is to be hoped that further investigation will lead to a still lessened cost of production in the future.

If a mixture of dead soft steel (i.e., with carbon content 0·1 per cent. or less) and carbon-free ferrochrome, in such proportions as to give a chromium content of about 14 per cent. in the mixture, be melted in a coke or gas fired crucible furnace, using the clay crucible which is commonly employed in the steel industry, it is quite likely that the carbon content of the resulting ingot will be 0·3 per cent. or more, instead of 0·1 per cent., or rather less as would be expected from the composition of the mixture charged.   If, instead of the mixture of mild steel and ferrochrome, a previously made stainless iron of like chromium content is melted in the same way, the carbon content of the melted material may be somewhat less than in the first case but it is likely to be 0·2 per cent. or thereabouts.   These increases in carbon content are due to the avidity with which metallic chromium, or its alloys with iron, absorb carbon from any carbonaceous matter with which they may come in contact while heated to

* British Patent, No. 135,187.   (10th November, 1919.)

high temperatures.   Thus the molten stainless iron absorbs
carbon from the crucible itself (the clay crucibles used in
steel manufacture are made from clay to which a small
amount of coke dust has been added) and also from the oxides
of carbon in the furnace gases, these oxides being reducible
by the chromium.   The higher carbon content of the material
melted from the mixture of mild steel and ferrochrome is
probably due to the greater reactive power of the latter alloy,
as compared with stainless iron, in decomposing the furnace
gases (with concurrent absorption of carbon) at tempera-
tures below melting point.

Partly on account of this carbon absorption and partly
on account of cost—the crucible process is the most expensive
commercial method of making steel—the basic lined electric
furnace is generally used for the production of stainless steel.
It may be suggested, of course, that it would be still cheaper
to employ the open hearth furnace.   The use of this type of
furnace, however, presents great difficulties, mainly owing to
the risk of seriously chilling the molten bath, due to the large
amount of ferrochrome which has to be added to bring the
chromium content of the bath to the required figure.

The procedure, when making stainless steel in an electric
furnace, depends to some extent on the charge.   If the
requisite chromium content of the steel is to be obtained
entirely by the addition of suitable ferrochrome, ordinary
steel scrap is first melted in the furnace and, if necessary, its
carbon content reduced to a low figure by means of an
oxidising slag.   The latter is then replaced by a non-
oxidising lime slag and the ferrochrome, and any other
necessary alloys, added.   Afterwards, the utmost precau-
tions have to be taken to avoid contamination of the bath
with carbonaceous matter, which is greedily absorbed by the
molten metal.   If, however, stainless steel scrap forms a
considerable part of the charge, the procedure is somewhat
different. · If attempts were made to reduce the carbon
content of the molten mixture by means of an oxidising slag
(for example, in an attempt to produce stainless iron from a
charge of higher carbon stainless steel), it would be found
that chromium was oxidised in preference to carbon ; the
chromium oxide so produced would form a bulky dry slag,
almost impossible to deal with in the furnace.   Generally,
therefore, when stainless steel scrap is remelted, no attempt

is made to reduce its carbon content ; a lime slag is used and oxidation of the chromium avoided as far as possible. One may note from this, the advisability of grading stainless steel scrap according to carbon content, or the value of low carbon stainless iron for remelting purposes is likely to be lost.

The type of ferrochrome needed to bring the chromium content of the bath to the required percentage will obviously depend on the carbon content required in the finished material, and also on the actual carbon and chromium content of the bath previous to the addition of the alloy. For the very low carbon stainless iron, only the practically carbonless alloy is of any use, but the somewhat cheaper grade of ferrochrome containing 0·5/1·0 per cent. carbon is generally suitable for the higher carbon steels, e.g., the cutlery quality containing about 0·3 per cent. carbon.

Owing to the high cost of the low carbon ferrochrome, and especially of the practically carbonless variety required for the production of stainless iron and other low carbon alloys, numerous attempts have been made to introduce the necessary chromium into the material at a less cost. One of the obvious methods is to use chromite directly in the steel-making furnace and by effecting its reduction there, eliminate part, at least, of the cost of the separate manufacture of ferrochrome. The actual reduction of the chromium in the steelmaking furnace, e.g. by means of aluminium or ferro-silicon, is feasible but the process presents a number of difficulties.

The use of aluminium as a reducing agent is familiar to most people in the " Thermit " process, used for example for welding tramway rails together on the track. A finely divided mixture of iron oxide and aluminium is ignited by a fuse which heats the mixture locally to a high temperature The reaction thus started is strongly exothermic and spreads rapidly through the whole of the mixture ; so much heat is evolved that the reduced iron is completely fluid and, flowing into the mould prepared to receive it, effectively welds the two juxtaposed ends of the tramway rails. If the oxide of iron be replaced with chromium oxide, a similar reaction is produced but it does not start so easily and when once started evolves much less heat. The expense of preparing a reasonably pure oxide of chromium from chromite would however be rather great and if attempts are made to use the

impure ore in the same way, the reaction is still more sluggish
owing to the rather large amount of inert oxides (alumina and
magnesia) present in the ore. These oxides, though not
partaking in the reaction, require to be heated up along
with the reacting bodies and their products. So sluggish
indeed is the reaction in this case that, if started locally by a
fuse, it will not propagate itself through a mixture of the
ore and aluminium ; the whole mixture must be pre-heated
in a furnace. If this is done, however, the ore is successfully
reduced ; thus a practically carbon-free ferrochrome may be
produced in this manner. The reaction also takes place
successfully if the mixture of aluminium and ore be added to
the steelmaking furnace. Aluminium, however, is decidedly
expensive and it also has the disadvantage that it reduces
any silica contained in the ore.

Silicon itself, in the form of ferrosilicon, is a cheaper
reducing agent. Its action is still more sluggish than that
of aluminium so that the mixture of ore and reducer needs
to be heated, e.g., in an electric furnace, to a high tempera-
ture before the two will react. It is quite possible, however,
to produce a low carbon ferrochrome in this way and patents
covering such a process were taken out in the United States
of America by E. F. Price and by F. M. Becket in 1907. In
1916, one of the author's colleagues, Mr. F. A. Melmoth,
successfully produced material containing 0·13 per cent.
carbon and 12·3 per cent. chromium in a 20 cwt. electric
furnace, the chromium being supplied entirely by the
reduction of chromite by ferrosilicon in the furnace.

The process, though possible, proved to be by no means
free from difficulties. Chromite is naturally not as free from
impurities as the purified alloy manufactured from it and
hence is more likely than the latter to cause trouble by the
introduction of these impurities into the bath or slag. In
addition, a rather voluminous slag is produced and this
lowers distinctly the output of the furnace and hence
increases melting costs. Again, the reaction has to be care-
fully controlled otherwise an excess of the reducing agent
may be absorbed by the molten metal and this, whether it
be silicon or aluminium, will have an effect on the mechanical
properties of the finished product which is very undesirable
for most of its possible engineering uses. In addition to
this, there is much more likelihood of variations in the

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composition of the finished steel when the chromium is introduced by this method than when it is added in the form of a definite weight of alloy of known composition.

The difficulties of the process are perhaps well illustrated by the numerous patents which have been obtained in connection with it, all of them claiming some special method of causing the reaction to occur or of controlling its course. It is not intended to give a resumé of all these attempts, many of which do not appear to have had much success ; it may be interesting, however, to refer to that modification of the process devised by Messrs. Hamilton and Evans* which seems to have achieved greater success than the others. The essential idea of this process is that the reaction occurs wholly in the slag, a layer of which is specially built up for the purpose. The function of this slag is to heat rapidly the mixture of ore and ferrosilicon which is fed into it, in order that the latter may be raised quickly to the temperature at which the reaction will commence. Hence there must be a sufficient bulk of slag and it must be very hot and fluid. The reaction mixture must not be fed into the furnace too quickly or it may chill the latter to such an extent as to prevent the reaction taking place. If, as is generally the case, ferrosilicon is the reducing agent, it is found that the reaction is favoured by the presence of sufficient lime in the slag to combine with the silica which is formed. Hence it is desirable that the special slag be as basic as possible, a condition which necessitates the process being performed in a basic lined furnace.

With the process under proper control, stainless irons containing about 12 per cent. chromium may be produced with considerable regularity as is evident from the analysis of a dozen casts made during the course of a " run " in a 8½-ton electric furnace and given in Table CXXXIV.† The production of higher chromium irons appears to involve difficulties which have not yet been completely surmounted. It is feasible however, to produce in the furnace by this method a molten metal containing 12/14 per cent. chromium and then to raise this chromium content to a still higher figure by the addition of a suitable amount of ferrochrome.

* British Patents Nos. 174,271 ; 198,323 ; 211,210 ; 213,737 and 262,206.

† The author is indebted to his colleague, Mr. F. D. Gordon for these analyses.

TABLE CXXXIV.

Analyses of Stainless Irons made by the Hamilton-Evans Process.

Heat No.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
1	0·09	0·40	0·30	12·0	0·23
2	0·085	0·34	0·32	11·5	0·26
8	0·095	0·31	0·28	11·8	0·25
4	0·10	0·33	0·27	12·1	0·26
5	0·09	0·47	0·30	11·7	0·23
6	0·085	0·47	0·32	12·6	0·22
7	0·10	0·51	0·31	12·7	0·26
8	0·085	0·42	0·31	12·0	0·22
9	0·085	0·37	0·30	11·9	0·26
10	0·09	0·35	0·30	11·7	0·24
11	0·10	0·38	0·25	12·5	0·25
12	0·09	0·42	0·29	12·2	0·23

What appears to be a modification of the Hamilton-Evans process, designed to limit the silicon content of the steel by regulation of the additions of ore and ferrosilicon, has been patented by R. and H. Wild.* In this process, ore is added in considerable excess of the theoretically calculated quantities. It is claimed that by this means, the silicon content of the steel is restricted to below 0·5 per cent. Against such an advantage must be placed the loss of chromium consequent upon the unreduced excess of chrome ore remaining in the slag.

The Hamilton-Evans process is generally worked in an electric furnace, probably because a sufficient excess of heat to carry the reaction through can easily be obtained in this furnace. Recently, however, it is stated that the process has been applied with considerable success to the open hearth furnace. Should such a modification prove to be a commercial possibility, it would very likely herald a notable reduction in the cost of stainless steels, a thing greatly to be desired because there is little doubt that one of the great handicaps to the more general use of these steels is their greater initial cost as compared with that of ordinary steel. The primary cost of an article is the one most frequently considered and although it has been found in practice that

* British Patent No. 198,423. (June 21st, 1922.)

for many purposes the relative cost of stainless steel, that is, its cost in terms of service and working life, is considerably less than that of ordinary steel, this point of view is often not sufficiently appreciated by potential users. A lessened cost of production is therefore to be desired. If, as a result of the adoption of direct reduction processes, the cost of manufacture of stainless steel is greatly cheapened, there is little doubt its application will increase rapidly.

The recent introduction of the high frequency induction furnace seems likely to solve the problem of the melting of small charges (e.g., five cwts. or so) of low carbon stainless alloys. It is possible in these furnaces to melt low carbon material without any appreciable absorption of carbon or loss of chromium and their commercial value in this respect has already been demonstrated. The high capital cost of the furnace has undoubtedly delayed its adoption for steel melting purposes, but a number of furnaces of 500/600 pounds capacity are already in operation in this country while on the Continent larger furnaces, holding one ton or so, have been installed.

Whatever method is employed for making stainless steels, and irrespective of the type of this steel which is being made, it is of the utmost importance that the bath and slag are in good condition before the metal is tapped from the furnace. The use of steel which is not perfectly killed leads to the production of ingots containing blowholes, with their accompanying spot segregates. This condition, as well as the presence in the steel of an abnormal amount of slag, is undesirable in any high quality material; but it is especially so in the case of corrosion resistant steel because the presence of heterogeneity lessens resistance to corrosion, a matter of much greater moment in these steels than in the ordinary variety. Articles manufactured from unsound or " dirty " ingots of stainless steel are more liable to pit in use than those made of sound, clean steel otherwise similar in composition.

The tapping of stainless steel from the furnace into the ladle and the teeming of the metal into the ingot moulds do not differ in any essential respect from the corresponding practices with ordinary steel. Owing, however, to the greater cost of the stainless material and to the trouble caused in later operations in manufacture and also after the material is put into use, by surface defects or by internal unsoundness,

it is of the greatest importance that every care and precaution be taken to ensure the ingots being as free as possible from avoidable defects.   The extra expense caused by such details as the use of properly designed ingot moulds with feeder heads, so as to eliminate piping from the body of the ingot, and the careful inspection of moulds to see that their surfaces are in good condition, is negligible compared with the saving obtained by their use.   In the same way the superior ingot surface obtainable in general by " bottom casting " makes it worth while to use this method providing, of course, precautions are taken to see that inclusions of ganister, firebrick, or other extraneous matter are not introduced through carelessness.

For the same reason, ingots of stainless steel which are intended for the production of bars or forgings on which little or no machining will subsequently be done, are almost invariably forged or rolled into blooms, the surfaces of which are examined most carefully for defects ; these, if found, are removed by machining.   The extra cost involved in such examination and machining is worth while both from the point of view of the steelmaker who wishes to supply a perfect product and also of the user who is thereby much less likely to have defective or unsatisfactory articles on his hands.

With the exception of the austenitic steels and the lowest carbon varieties of the plain chromium steels, stainless steels air harden intensively on cooling from high temperatures.   Care must therefore be taken with the cooling of the hot ingots, otherwise serious cracks may form as a result of too rapid or uneven cooling.   In addition to this, if the material becomes hard when cold it is then much more susceptible to cracking during after treatment.   Cracks are produced much more easily in hard than in soft steel by rough handling or grinding.   The latter, if done rashly, causes local heating and the expansion due to such heating may easily set up sufficient stress in the neighbourhood of the heated area to cause cracks to form in hard non-ductile material.   Similarly, surface defects are much more dangerous as starting points of cracks when they occur in hardened steel. Finally, when the ingots have to be reheated for forging or rolling operations, much more care is required to prevent cracking occurring if they are in the hardened condition.

The most certain way of avoiding or, at least, greatly

minimising these troubles is to take care that the material is never allowed to become hard either in the ingot form or between the various operations of reheating and forging or rolling. As this point is of the utmost importance in the manufacture of those types of stainless steel which are capable of air hardening, it is necessary to emphasise it thoroughly, and no excuse is required for going into some detail with regard to the methods of preventing the trouble.

Forging and Rolling.

It will have been realised that the term " stainless steel " covers a large range of materials having widely different properties. From the point of view of forging or rolling operations, and particularly with regard to air hardening characteristics, the various steels may conveniently be divided into four groups, as follows :—

(1) Steels which harden intensively on air cooling from forging heats. This group embraces the chromium steels of the " cutlery " type containing up to about 15 per cent. chromium and more than about 0·10 per cent. carbon. It also includes those steels of higher chromium content (e.g., 16/20 per cent.) which possess sufficient hardening capacity, due either to fairly high carbon content or to the presence, in sufficient amounts, of other alloying metals, e.g., nickel.

(2) Low carbon chromium steels of the " stainless iron " type. These harden to some extent when air cooled from forging heats but generally to a Brinell hardness number not exceeding 300/350. There is no sharp line of division between this group and the preceding one, the two forming a continuous series.

(3) The austenitic chromium-nickel steels of the " Anka-Staybrite-V.2.A " type.

(4) The complex alloys and those of high nickel content ; these are generally austenitic and include many of the heat resisting alloys.

In most cases, when dealing with these steels, forging or rolling operations are conducted on material which has been reheated to some temperature between 1,000° and 1,200°C. If steels in group (1) are allowed to cool freely in the air after the forging or rolling operations are completed,

they will harden intensively. Those of group (2) will harden to a less extent depending on their composition. Steels in groups (3) and (4) will not harden at all under the same conditions. Bearing in mind what was stated in the three preceding paragraphs, it will be convenient, before dealing with the actual forging or rolling operations, to consider first the precautions to be adopted with steels of group (1) in order to prevent cracking, due to hardening. These precautions will apply also, to a modified extent, to the irons of group (2) but are not necessary or even desirable with the austenitic steels of groups (3) and (4).

When the material is allowed to cool after forging or rolling, this should be done in such a way that the air hardening tendency is, if possible, completely suppressed. The material when cold, is then in the pearlitic or annealed condition. For this purpose the hot bars, blooms, billets, or whatever form the material is in, may be allowed to cool slowly in some form of furnace or firebrick-lined pit. In ordinary stainless steel of the straight chromium type, the carbon change point generally occurs in the range 600°/750° C. on slow cooling. The material should therefore be allowed to cool slowly over this range of temperature. The rate of cooling down to 750°C. is immaterial, but from 750°C. to 600° C. the rate of cooling should not be faster than 50° an hour at the most. If the cooling through this range has been done efficiently, the material may then be safely cooled either quickly or slowly and will be soft.

If the content of nickel in a hardenable steel is fairly high, e.g., more than about 1·5 or 2·0 per cent., the change from austenite to pearlite at Ar.1 may take place so sluggishly as to require the steel to be kept for 24 hours or more at the requisite temperature, thus making the commercial annealing of such material in the manner suggested above, well nigh impracticable. It is advisable, however, after forging or rolling such steels, to cool them slowly down to atmospheric temperature in order to minimise the dangers of cracking. It cannot be too strongly emphasised that when steel hardens either at rapid or slow rates of cooling, it undergoes a structural change in the neighbourhood of 200°/400° C., which is accompanied by a considerable expansion of the metal. For example, Fig. 216 represents the change in length of a bar, 4 inches long, of a strongly air hardening

stainless steel during cooling from 1,000° C. Down to about 300° C. the material contracts in a perfectly regular manner. Between 280° C. and 140° C., the structural change producing hardening takes place and is accompanied by a
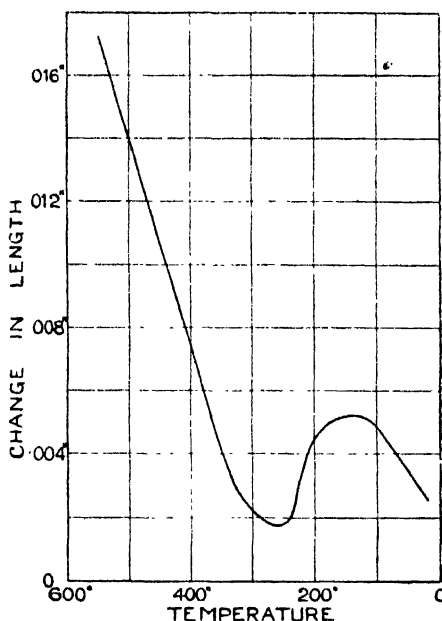
Fig. 216. Change in length of bar, 4 in. long, of air-hardening steel on cooling from 1,000° C., showing expansion at lowered change point.

0·23 per cent. carbon ; 17·5 per cent. chromium ; 2·42 per cent. nickel.

notable expansion, amounting to about 0·1 per cent. of the length of the sample. If the length which the bar would have attained at 140° C., had it continued to contract down to that temperature at the rate it possessed above 300° C. be taken into account, however, the effective expansion is about three or four times the value given above. At a temperature of 140° C., hardened steel is almost as rigid as at atmospheric temperature ; it will not distort appreciably under stress and if attempts are made to cause it to distort, it will very probably crack. If a bar or forging of such steel as is represented in Fig. 216 cools down slowly and uniformly after forging or rolling, all parts of it will have the chance of passing through the hardening range at approximately the same time and hence, as the different parts of the article expand or contract together, the likelihood of internal

stresses being set up in it is at a minimum. On the other hand, should the forging be allowed to cool down more or less rapidly on the shop floor, it is certain that the outer layers will have passed through the hardening change and will have become relatively rigid by the time the inner parts reach this change and commence to expand. The result is the development of considerable tension in the outer layers and compression in the inner parts, a condition very apt to lead to the formation of cracks. Temperature differences during cooling are accentuated if the forging is of uneven section ; the danger of cracking is correspondingly increased.

It may be asked why so much emphasis is laid on the dangers of cracking during air cooling from forging heats when the same type of material is regularly air-hardened from temperatures of 950° C. or so during heat treatment operations. If the steel may be safely air-hardened as a part of its heat treatment, why may it not be air-cooled after forging or rolling with equal safety ? The answer is that the likelihood of cracking in the two cases is simply a question of degree ; cracks are not unknown in heat treatment operations, as many know to their cost, but there are several weighty reasons why they are less likely to occur in such operations than during cooling from forging or rolling heats. Thus, during the heat treatment of an article, care is taken to ensure that it is heated as evenly as possible before it is drawn from the furnace to cool in the air and, during cooling, the experienced operator will see that it is shielded from draughts, so that unnecessary temperature inequalities are avoided as far as possible. On the other hand, the temperature of a forged or rolled article, immediately after these operations are completed, is likely to be far from even, due among other things, to the cooling effect of contact with the hammer faces or the rolls ; and unless the forge or mill is specially laid out for the purpose, there is not the same opportunity, as in a heat treatment shop, for allowing the hot forging or bar to cool undisturbed by air currents. Both these conditions increase the temperature gradients of the forged or rolled article as compared with that heat treated, and thus increase the risk of cracking in the former. Again, the structure of a heat treated article is, or should be, in its best possible condition ; that of the forging on the other hand is likely to be coarser and hence not so strong mechanically ;

and every smith knows that a tool overheated during hardening is more fragile than one properly treated. Finally, most articles made of air-hardening steels are machined, to remove all surface defects, during the progress of their manufacture and hence, when they reach the heat treatment stage, possess a sound skin, free from seams, laps and roaks ; a condition of affairs seldom obtained in a forging before it has had this necessary machining. Small surface defects are very prone to act as the starting points of cracks, because they act as so many sharp notches and intensify locally the stresses set up as a result of cooling. In view of all these adverse conditions, it is not surprising that forgings or rolled bars are much more liable to crack if they are allowed to cool in the air after forging or rolling is complete than are articles of the same steel during air hardening operations in the course of normal heat treatment processes. The whole matter is, however, one of degree and it is possible, if attention be given to the points mentioned above, to combine the final forging or rolling of a small article with its first heat treatment operation ; that is, to air cool such an article after forging or rolling and subsequently merely to temper it in order to obtain required physical properties.

Although the method of cooling in a firebrick-lined pit may be satisfactory when the material is in the form of very large pieces which retain their heat for hours, it is an unsatisfactory method for small billets, bars or forgings which cool more quickly. A far better method for such small-sized material is to charge the hot forgings or bars into a furnace which is kept in the range of temperature in which the carbon change occurs on slow cooling and hold them in this range for a sufficient length of time for the change to take place. After this has occurred, the material can be air-cooled or even quenched in water and will still be quite soft.

In practice, it is better to adopt 600°/700° C. for the furnace temperature, because most samples of hardenable stainless steel contain small amounts of nickel, and this element lowers the maximum temperature at which the change point can occur. It is obviously no use holding the steel at a temperature above the highest at which the carbon change can possibly take place whereas the use of a temperature 50° or 100° C. below this highest value is perfectly successful.

Except in the case of the hardenable stainless steels containing relatively large amounts of nickel (e.g. steels of the " Twoscore " type) for which this method is not so suitable, and for obvious reasons, soaking for about an hour in this range of temperature is generally sufficient to cause the carbon change to take place completely ; it is advisable, however, to have some means of knowing when the red hot material has actually changed from austenite to pearlite. For this purpose, one may make use of the fact that the steel becomes magnetic when this transformation takes place. The steel should be tested with a small permanent magnet and should be allowed to stay in the furnace until it is distinctly magnetic while it is red hot.   It is, of course, no use applying the magnet test after the steel has gone cold, as it is then magnetic whether hard or soft.

It should be noted that the magnet test mentioned above, while perfectly satisfactory for stainless steel, is not a reliable criterion of the annealing of the low carbon material, stainless iron.   Separation of free ferrite occurs in this material during slow cooling, at a temperature above that of the carbon change point, in a similar manner to the separation of free ferrite in ordinary mild steels.   The free ferrite which has thus separated out undergoes the Ar. 2 magnetic change at a temperature of about 650°/680° C., and hence will be decidedly magnetic immediately after this change has occurred, although the rest of the structure (which contains the carbon) is still in the form of non-magnetic austenite and therefore capable of forming either martensite or pearlite, depending on the subsequent rate of cooling.   Such mild material, however, has only a moderate hardness after air cooling (generally of the order of 230/320 Brinell) and hence is much less susceptible to cracking and other defects liable to be produced in material which air hardens intensively.

This method of annealing hardenable stainless steels by holding them in the range 600°/700° C. has proved of great value in their manufacture and working, especially when in the form of small articles. During the production of small drop stampings, for example, the hot stampings should be charged, as soon as the stamping operation is completed, into a furnace kept at 600° to 700° C., and allowed to soak, after which they may be air cooled with perfect safety.   It is of no consequence if the stampings are actually below 600° C.

when they are charged, providing they are not lower than about 350° C., except that the process will take longer owing to the time taken to reheat them to the necessary range of temperature. If the temperature is below about 350° C,, the lowered carbon change point, resulting in the production of hardened material, may have taken place partially or completely, with the consequent liability for cracking to occur. For material cooled to such a temperature, reheating to 600°/700° C., followed by soaking at that temperature would result, of course, in tempering the hardened steel.

As troubles due to cracking become evident when the material becomes cold, obviously one way out of the difficulty is to prevent the articles cooling down between successive stages in the working of the steel ; thus the material may be charged back into the reheating furnace immediately one stage of the forging operation is completed (for reheating for the next operation) whilst the bloom, billet, or whatever form the material is in, is still red hot. As a preventative of cracking, this method, when properly carried out, is satisfactory. It has the disadvantage, however, that there is no opportunity (as the material does not become cold between these successive operations) for examination and removal of defects, e.g., by chipping or machining, between the forging operations.

This method is of value, however, in dealing with ingots when conditions will allow it to be applied. Owing to structural characteristics, stainless steel, like other steels, will probably crack more easily in the ingot form than after being worked, so that, if the rolling or forging procedure will allow it, it is an obvious advantage to keep an ingot hot until it has been forged or rolled (and therefore not give it any chance of cracking) rather than to cool it even under conditions which would soften it perfectly. It is well to remember that even when fully annealed, cold ingots of hardenable stainless steels should be treated with as much care as an ingot of, for example, file steel.

As stated earlier, all these precautions relate to the hardenable forms of stainless steel. They are not necessary when dealing with the austenitic varieties or with the high chromium stainless irons which do not air harden appreciably.

The forging and rolling of steels of groups (1), (2) and (3) is carried out in much the same way as that of ordinary steel

except that they need more care than the latter. Generally speaking they are more "tender" than ordinary steels, especially during the early stages of the working of ingots. Thus, ingots 12 or 14 inches square may sometimes be rolled down to billets in the same way as ordinary steels, but often it is preferable to cog the ingot, under the hammer or press, as by so doing there is less risk of cracking or tearing it. After this preliminary cogging, the blooms may generally be rolled or forged in much the same way as ordinary steels though, owing to their greater hardness, they may admit of less reduction per pass or less work per heat than mild steel. Also they spread to a different extent ; hence it is often necessary that passes in rolls for producing small sections be arranged differently for stainless steels as compared with ordinary steels.

Stainless steels, as a class, are considerably harder than carbon steels ; thus stainless iron forges with about the same ease as ordinary steel containing 0·4 per cent. or so carbon ; forging becomes more difficult as the carbon content of the stainless steel increases so that the harder varieties of group (1), with carbon about 0·4 per cent. or over, are almost as difficult to forge as high speed steel. The difference between stainless iron and the grade suitable for cutlery (carbon about 0·3 per cent., group 1) is illustrated by the fact that four to six times as much work may be done on the former material at one heat as on the latter. Stainless iron may be hand forged quite easily into small articles, even of complex shape such as spurs, but a power hammer is indispensable for larger articles or for those made of the harder varieties of group (1).

The irons and steels of groups (1) and (2) may be forged quickly and by rapid blows between temperatures of about 1,200° C. and 900° C. without danger of splitting. Below 850°/900° C., they stiffen up considerably and if attempts are made to deform them forcibly by heavy blows, they will be unduly stressed and may crack. There is more latitude with regard to the softer irons ; thus the rolling of small sections of these materials may often be continued down to lower temperatures, e.g., 700°/800° C., if necessary.

The austenitic steels of group (3) are at least as hard at forging temperatures as those of group (1). They also may be forged or rolled between temperatures of about 1,200° C., and 900° C. Below 900° C. they stiffen up very markedly

and forging or rolling below this temperature should.generally be avoided.   Hot working operations become more difficult with steels of group (4) ; these more complex alloys, formed by adding other metals to the chromium-nickel steels of group (3) are in general more tender than the latter.   They are prone to cracking and often need to be worked with great care.   Many of these alloys, especially· those of the heat resisting type possessing great strength at high temperatures, are much harder at forging or rolling heats than are the simpler steels of groups (1), (2) and (3) ; they would not serve their purpose if they were not.   Hence they require lighter reductions in rolling operations than the simpler steels and more frequent reheating in order to carry out a given amount of hot working.   Often they are only available commercially in the simpler worked shapes.   For example, they may be rolled into round or rectangular bars but often the production of thin sheets or of special sections, such as those for turbine blading, is difficult if not impossible ; nor can they usually be pierced or rolled into seamless tubes.

Stainless steels and irons of groups (1), (2) and (3) may be drop stamped between temperatures of 1,000° to 1,200° C. Whenever possible, it is better to use stainless iron or the milder types of the steel rather than the higher carbon grades, as the former flow more easily and hence cause less wear and tear of the dies.   It is also advisable to do as much of the work as possible in preliminary shaping dies.   They may also be swaged without any unusual danger of causing the centre to split and may be upended, providing this process is not carried too far in one operation without reheating. Laps should be particularly avoided in hardenable steels, as cracks may start from them when . the stampings harden subsequently on air cooling.   The fash should be cleaned off stampings of these steels whilst they are hot ; should they have been allowed to cool without this having been done, they should be reheated to a low red heat and the fash then cleaned off.   If these precautions are not carried out, cracks are very likely to form along the fash ;   thus many table knives are cracked on the heel and bolster because this effect of the fash is not realised.

Finished stampings or forgings of the hardenable steels should not be thrown on to damp floors or in places where considerable variations in cooling rate may occur.   If the

forgings are of simple form, they may be cooled out of draughts and preferably.in a warm place. When cold, they will be more or less hard, depending on composition and may require annealing or tempering before any machining can be done on them. Forgings of intricate pattern, especially those made of the harder varieties of stainless steel, should preferably be charged after final forging, into a furnace at 600°/700° C. and annealed as described on page 474.

Although the forging or rolling of stainless iron and the hardenable stainless steels which have been heated to ordinary forging temperatures (1,000° to 1,200° C.) should not as a rule be continued below 850°/900° C., owing to danger of cracking, it is practicable to work small sections from an initial temperature of about 750° C., i.e., below the Ac.1 change point. When thus heated, such stainless material flows without danger of cracking, but requires very heavy pressure so that probably few mills or forging appliances are powerful enough to deal with bars finishing greater than about a square inch in cross section. After being worked in this manner, the material may be air cooled without danger, because it will be soft when cold, due to the initial reheating temperature being below Ac.1. Bars so rolled or forged have a very fine surface ; this is particularly the case if the billet, from which the bar or article is to be rolled or forged, is pickled free from scale before it is reheated for the final rolling or forging operation. The subsequent heating to 750° C. or thereabouts produces only a very thin film of oxide on the surface and hence the final surface has only an exceedingly thin scale, easily removable by a very short pickling operation. The whole process is somewhat in the nature of cold working in that the crystals of the material are distinctly elongated in the worked bar and the tensile strength of the latter is raised somewhat by the process. Moreover, bars rolled in this way have a very high impact value. In order that the operation may be successful, the temperature of the material must be carefully controlled, because if the limits given above are exceeded the material may prove defective. For this reason the process is likely to be of greater value to the steelmaker who wishes to produce small bars or strip or sheet, and has every facility for controlling temperatures and the necessary technical staff for supervising the process, rather than to the general user of stainless material. When the necessary control is available,

however, the process is exceedingly useful.   For example, the heading of small bolts could be carried out by this means and if the bar stock had been previously hardened and tempered to give the required tonnage, no further heat treatment operation would be necessary on the headed bolt. Although the method of low temperature rolling may be used with all grades of non-austenitic stainless material, it is particularly applicable to stainless iron owing to the greater softness of this grade at the rolling temperature. In addition, when the iron has a high chromium content, e.g., 14 or 16 per cent., the rolling temperature may be increased to 800° C. with safety because in such material the Ac.1 change occurs at a higher temperature than in the ordinary types of stainless steel.   It may be added that for all such low temperature rolling or forging operations, perfectly sound material is necessary.   For example, bars rolled in this way from billets prepared from piped or blown ingots are very liable to split longitudinally during the rolling operation.   Those who wish to use the process at all should take care, therefore, that they obtain perfectly sound material such as can only be ensured by skill and care in the melting and casting operations as well as in the subsequent rolling or forging of the ingot.

It is not generally advisable to roll the austenitic chromium-nickel steels under these conditions.   They are much more rigid at such temperatures than are the hardenable steels and therefore more difficult to work.   Also, they are not so ductile in the range 600°/900° C. as at higher temperatures owing to the separation of carbide films round the grains: The loss in ductility is greater, the higher the carbon content, as is evident from Fig. 217 ;   it also seems to occur more readily with a higher chromium content (e.g. 20 per cent.) than with a lower (e.g. 15 per cent.)   If such a process should be used, however, for any of these austenitic steels, the material must be heated, after forging, to a temperature of 1,000°/1,200° C., depending on composition, and rapidly cooled, otherwise its resistance to corrosion is seriously diminished ;   see pages 276 *et seq.*

It may be convenient at this point to refer to riveting operations and other processes used by boilermakers in the construction of plant.   Rivets of stainless material are generally of two types, stainless iron or the softer austenitic chromium-nickel alloys of the "V.2.A." class ;   as a rule, they

should be made of the same type of material as the plates for which they are to be used, in order to avoid electrochemical effects.*   Ordinary mild steel rivets are particularly " fool-proof " ; when being driven, they· may be heated up to
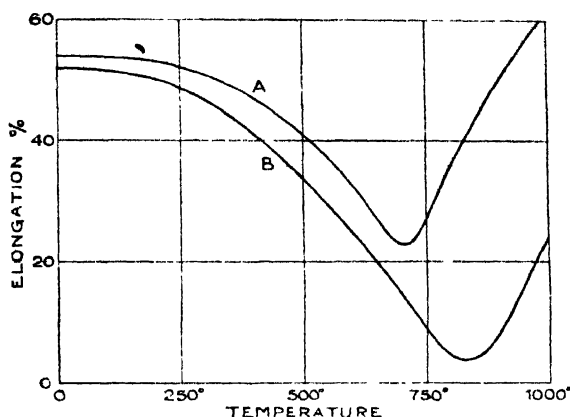
Fig. 217.   Change of elongation with temperature in tensile tests at high temperatures on austenitic steels.   (Strauss.)

Curve	Carbon %	Chromium %	Nickel %
A	0·17	20	7
B	0·45	19	6

temperatures of 1,300° C., or even higher, and providing the steel is not actually burnt and the rivet is properly closed, the engineering profession considers the operation satisfactory. As a result, the heating of rivets is probably the least skilled job in a boiler shop ; often it is carried out by the youngest boy in the place.   Riveting operations with rivets of one or other type of stainless steel, however, demand more care ; perfectly satisfactory rivets may be driven using material of either the stainless iron or the austenitic groups, but certain details must be attended to or the resulting rivet may either be weak mechanically or have its resistance to corrosion impaired.

The rate of cooling of the hot rivet, when driven, is

* More freedom is possible where nitric acid is concerned ; both laboratory experiments and plant tests indicate that electrochemical effects are not produced, for example, between 16/18 per cent. chromium irons, and the austenitic steels of the " V.2.A." type of similar chromium content when they are in contact with this acid.   It would be possible, for example, to use rivets of the latter steels with plates of the high chromium irons in nitric acid plant.

relatively fast—distinctly faster than that of the same rivet cooled freely in the air—owing to the cooling action of the plates into which it is driven.   Hence if rivets of stainless iron, containing up to about 14 per cent. chromium, are heated, for driving, to temperatures above 800° C., they will harden appreciably on cooling and be more or less brittle. Irons with a higher chromium content, e.g. 16 or 18 per cent. do not harden to the same extent as those with less than 14 per cent., but they are noticeably more brittle when quickly cooled from temperatures which would harden a lower chromium iron than from 800° C. or lower.   Hence, rivets of stainless iron of any description should not, as a general rule, be heated to temperatures above 800° C., when they are being driven, or the heads are liable to fly off when they are stressed, e.g., during heavy caulking operations. If, on the other hand, the rivets are heated to a temperature not exceeding 750°/800° C., that is below the Ac.1 point, they will not harden on cooling, no matter how fast the rate. Hence rivets of the lower chromium irons, when treated in this way, retain their usual great toughness while those of high chromium content are less brittle than they would be if cooled from higher temperatures.

The driving of stainless iron rivets from a temperature of 750°/800° C. presents no trouble when a hydraulic riveter is employed, but may cause some difficulty if small pneumatic hammers are used or if the rivets are hand driven.   In these cases, if a higher temperature is essential to enable the rivet to be closed properly, a little more latitude in this direction may be obtained by carefully selecting tough material which does not harden greatly when air cooled from temperatures up to 900° C. or 950° C.   The most promising type of com-position appears to be about 14 per cent. chromium with carbon as low as possible ; also, the nickel content should not be unduly high.   Such material does not harden nearly so much, under the conditions mentioned, as iron of lower chromium content ; at the same time, like the latter, it possesses a great degree of toughness, a quality which is generally lost when the chromium content reaches about 15 per cent.   An exception to this is found, however, in the special high chromium iron, " Brearley K " brand, manu-factured by Messrs. Brown, Bayley's Steel Works Ltd. Rivets of this material, containing 16/18 per cent. chromium,

may be driven at temperatures of 900°/950° C. and still possess a reasonable amount of toughness.

The necessity for using a low temperature does not arise when rivets of the austenitic chromium-nickel steels are employed. On the contrary, such rivets must not be driven at 750°/800° C. or their resistance to the corrosive attack of many chemicals is likely to be seriously reduced. Also, rivets of such steels must not be heated locally ; the whole rivet should be heated to 1,100°/1,200° C. and then driven as quickly as possible. If only the end of the rivet is heated to these temperatures, some part of shank will obviously reach a temperature of 500°/900° C., i.e. that range of temperature which causes precipitation of carbide round the grains of the austenite, leading to the intergranular disintegration of the steel if it be exposed to the attack of many chemicals, as described on pages 276 *et seq.* Such a condition might easily be fatal to the life of rivets used, for example, in the construction of chemical plant.

Austenitic steel used for rivets should have as low a carbon content as possible ; this is advisable not only on mechanical grounds –low carbon steels being softer and therefore more easily worked than those of higher carbon content—but also in regard to corrosion resistance. The higher the carbon content, other things being equal, the more rapid the rate of cooling from high temperatures necessary to prevent precipitation of carbide films.

It might appear from these remarks that rivets of austenitic steels are easier to use than those of stainless iron ; actually, however, the former are so stiff and hard to deform at temperatures below about 900° C., and in addition harden up so rapidly if forcibly deformed at lower temperatures, that unless an austenitic rivet is rapidly driven and well closed before its temperature falls much below about 900° C., it may be found difficult, if not impossible to close it at all.

The necessity for controlling rather carefully the temperature of riveting will doubtless be considered by many boilermakers to be a distinct drawback to the use of stainless steels. Undoubtedly the heating of rivets of these steels will require more care than those of ordinary mild steel usually receive. The extra care is necessary, however, and although the future may possibly see the production of types of stainless steels possessing greater flexibility in this respect,

it is doubtful whether any material of this type will be produced which will be quite so " foolproof " as ordinary dead mild rivet steel.

Caulking operations do not present any difficulty. with stainless irons ; they are as easily carried out as with mild steel.   The austenitic steels are more difficult on account of their work-hardening tendencies ; when riveted joints are to be made in these steels, the plates to be riveted must fit closely together and the riveting be well done, otherwise it may be impossible to produce a really tight joint.

In the fabrication of vessels and other plant by boiler-makers' methods, it is frequently the practice to reheat plates to possibly 700°, 800° or 900° C., in order that such operations as flanging and bending may be carried out more easily.   Similar methods may be used for stainless irons or the austenitic steels, providing the effects of heating to such temperatures on the properties of the materials is borne in mind and also the necessity, in most cases, of a final heat treatment in order to correct these effects.   Stainless iron plates, intended for the manufacture of large vessels of various kinds, are generally tempered at about 700° C., after rolling in order to soften them and make them as tough as possible.   Reheating such plates to 700° or 750° C. for fabrication purposes, will not affect their properties to any noticeable extent ; if, however, they reach temperatures of 800° C. or over, they will afterwards harden to a greater or less extent, depending on their subsequent rate of cooling. Plates so treated should be re-tempered at 700° C. or thereabouts in order to restore their toughness.   If, on the other hand, the rate of cooling from 800° C. or over had been rather slow, the plates would become more or less annealed ; in this case, a subsequent tempering operation would assist in toughening the finished plate but would leave it softer than it would have been in the hardened and tempered condition, an effect which might, or might not, be of any real importance.   The extent of the softening may be judged by a comparison of the tests already given for annealed as against hardened and tempered stainless iron.

Whether heat treatment is necessary or not on an austenitic steel article which has been reheated to 1,000°/1,200° C. for some fabrication process will depend on circumstances.   The determining factor in this case

is the rate of cooling between 900° C. and 500° C. If the process is such that it may be completed before any part of the steel has fallen below 900° C., so that the fabricated article may then be air cooled or quenched in water, depending on its thickness, subsequent treatment will not be necessary. If, however, the process cannot be so completed, and as a result the cooling of the steel is retarded between 900° and 500° C., subsequent treatment is essential.

In the case of the austenitic steels, any reheating to temperatures of 500°/900° C. for fabrication purposes must be followed by a final reheating to a temperature of 1,000°/ 1,200° C. with rapid cooling therefrom ; or the resistance of the steel to the attack of chemicals is likely to suffer very seriously. Final heat treatment is also necessary if the steel has been locally heated, even to temperatures of 1,000° C. and upwards ; there will always be some part of the plate or other article which has reached a temperature of 500°/900° C. only and is thus in an unsatisfactory condition.

Welding. No type of stainless steel can be welded at the smith's hearth in the same way as ordinary mild steel ; probably all types may be welded electrically, by means of the oxy-acetylene blowpipe or by the Atomic Hydrogen process, though not with equal ease. The operation is more easily carried out with the austenitic chromium-nickel steels than with other types of stainless steels, while material with high chromium (and low nickel) probably gives most trouble. Stainless irons are more easily welded than hardenable steels of like chromium content and, of the latter, as with ordinary carbon steels, the higher the carbon content the greater the difficulty in welding. In all cases, more care is required than when handling ordinary mild steel and certain precautions are necessary to obtain satisfactory welds. In addition, the local heating of the steels to their melting point produces certain structural changes in the neighbourhood of the weld which are undesirable, rendering subsequent heat treatment generally necessary. It will be convenient if the actual welding operations are first considered and afterwards the structural changes produced and the effects of these.

In all cases the stainless material to be welded must be free from scale ; if not machined, it should be pickled or sand-blasted. Stainless steels are more resistant than

ordinary steels to oxidation when heated to high temperatures, but the scale which forms on them is much more refractory. It does not readily unite with fluxes to form a slag which will melt and leave the metal clean to unite with the welding rod or piece to which it is being welded. Probably it is largely due to this fact that stainless materials cannot be welded at the smith's hearth.

When using the oxy-acetylene blowpipe, a slightly reducing flame must be used ; if oxygen be in excess, the metal will be oxidised, giving porous welds such as that shown in **Fig. 218.** The cavities here shown are due to gas formed by the reaction between the oxide produced and the carbon in the steel. On the other hand, the acetylene must be only slightly in excess or the weld will be highly carburised and, as a result, hard, brittle and less resistant to corrosion. The ideal condition would be to use a neutral flame but, as this is not easy to obtain, it is best to have a slight excess of acetylene. The flame should be adjusted so that the small blue cone, which is produced at the jet when oxygen is in excess, is just replaced by a small luminous cone. An undue excess of acetylene must be guarded against as it is a very natural fault. The observant welder will soon notice, that when using a good excess of this gas, the welding rod melts very cleanly and runs easily ; moreover, the weld can be built up in several layers much more easily than when a less reducing flame is used. As, however, the highly carburised welds thus produced are much less resistant to corrosion than those of lower carbon content and are also harder and less tough, they must be carefully avoided.

The flame should be directed along the joint to be welded so that the parts being heated are continuously bathed in the flame, this preventing oxidation. As regards welding rod, the austenitic chromium-nickel steels should be welded with their own material ; this also applies to the special complex alloys formed from these and to those of high nickel content, such as " Rezistal," " Hotspur," and the " ATV " alloys. Welding rod of these higher nickel alloys has a lower melting point and flows somewhat more readily than that of the lower nickel material (e.g. " Anka " or " V.2.A.") ; on this account it may be used occasionally for welding the latter steels in cases, e.g. domestic articles, where it is not likely to lead to corrosion troubles. The high nickel rod should not be so

Plate XLVI
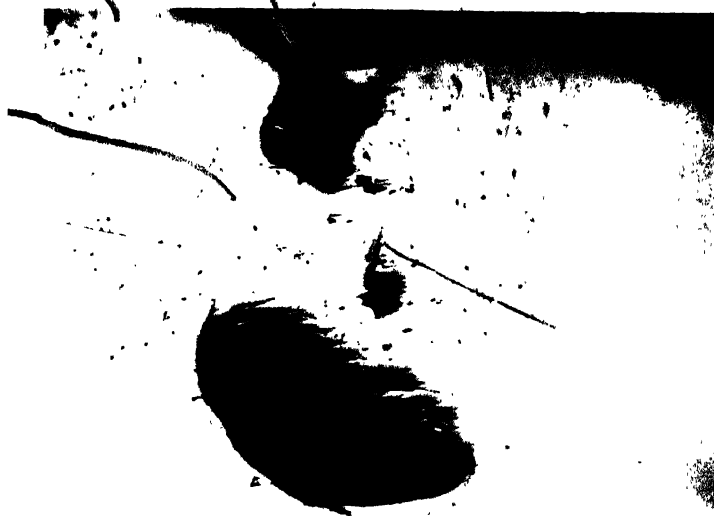
Fig. 218.— Porous weld due to oxidising flame.   100.
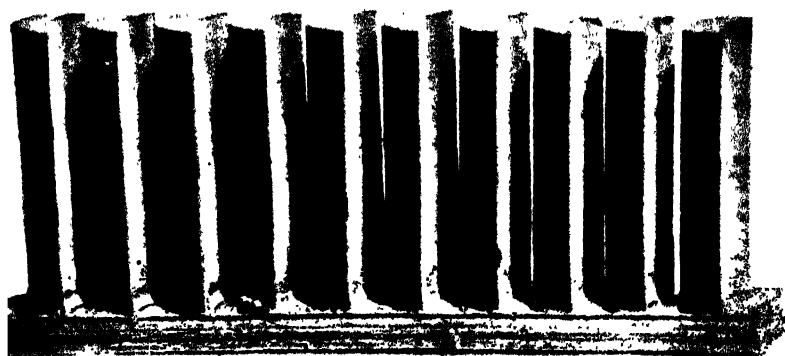
Fig. 219.— Group of small stainless iron turbine blades oxy-acetylene welded to a mild steel ring. Slightly enlarged.

Plate XLVII

Fig. 220. Section through one of the joints in Fig. 219.   15
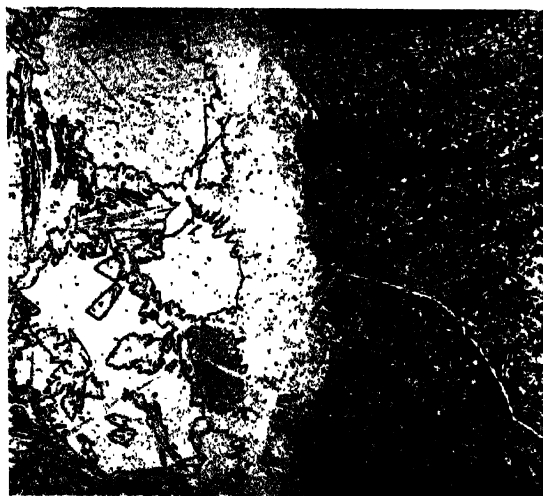
Fig. 221. Part of the weld shown in Fig. 220, magnified 100 diameters, showing the junction between the stainless iron (left hand) and the mild steel.

Plate XLVIII
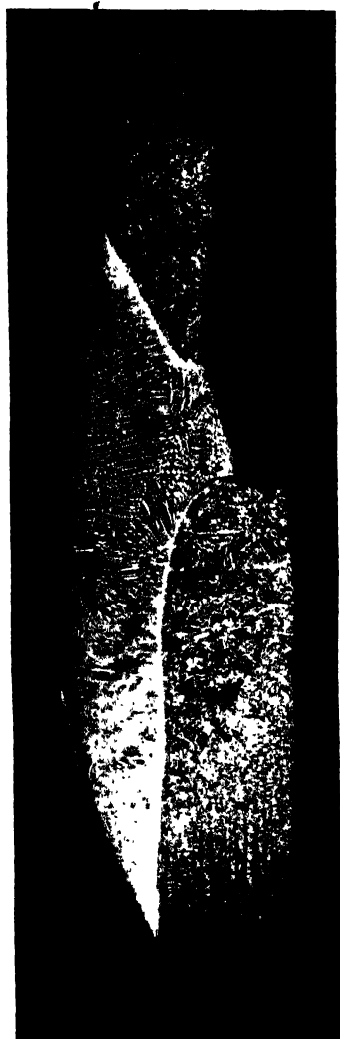
FIG. 222. Lap weld (oxy-acetylene) between two pieces of 18-gauge stainless iron sheet. The special stainless welding rod mentioned on page 487 was used for this weld.   18

Plate XLIX

Fig. 223. Part of the weld shown in Fig. 222 magnified 750 diameters, showing the junction between the stainless iron (left hand) and the welding material. Note the grain boundaries crossing the weld, indicating metallic continuity.
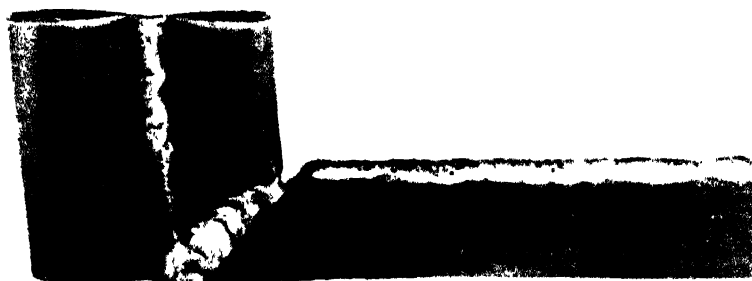
Fig. 224. Welded " Anka " tube, flattened after welding.

used in the construction of vessels or plant intended for chemical work as the difference in composition may cause electrochemical action ; in particular it must not be employed when the welded vessels will come in contact with nitric acid as the high nickel material is distinctly attacked by this acid (see Table LXXX, page 351).

The plain chromium steels and irons, and also those more or less hardenable which contain small quantities of other metals, such as nickel, copper, tungsten and silicon, cannot as a rule be effectively welded with filler rod of similar composition to themselves.   Generally the best rod to use is the high nickel-chromium material of the " Hotspur " type (15/20 per cent. chromium, 20/25 per cent. nickel) as this flows readily.   When joints are being made between these stainless steels and carbon steels, ordinary mild steel welding rod may be employed quite satisfactorily.   Fig. 219, for example, shows a group of small turbine blades of stainless iron welded to a mild steel ring.   In this case, the material of the ring formed the welding rod and Figs. 220 and 221 representing respectively a section through one of the welds, and the actual junction of the stainless iron and mild steel at a higher magnification, show that welding of the two materials has really taken place ; there is no sharp line of division between them.   Similarly, Fig. 222 represents a section through a lap weld between two sheets of stainless iron for which " Hotspur " welding rod was used ; Fig. 223 taken at a much higher magnification at the junction of sheet and welding material indicates, by the fact that the grain boundaries cross this junction, that a very definite union between the metals has taken place.

The tube reproduced in Fig. 224 was made from " Anka " sheet, bent to shape and then welded ; it was subsequently flattened along the joint and the photograph illustrates the toughness and ductility of the weld, a characteristic feature of these austenitic steels.

What is probably the main difficulty in oxy-acetylene welding, namely correct adjustment of the flame, is entirely avoided in the Atomic Hydrogen welding process.   Dr. Langmuir discovered some years ago that if hydrogen were heated to a sufficiently high temperature, it dissociated into the atomic form.   On cooling down again the atoms recombined with development of heat and conditions could be

arranged so that an intensely high local temperature was
produced.

In the application of the method to welding, a stream
of hydrogen is directed through an arc maintained between
two small tungsten electrodes.   The hydrogen is largely
dissociated, and this dissociated stream is directed at the spot
to be welded.   Recombination of the atoms to the molecular
form seems to be aided catalytically by iron, steel and other
metals and, as a result, an intense heat is produced where
this stream impinges on to the metal to be welded.   Both
calculation and experiment indicates that the temperature
reached is considerably higher than that of oxy-hydrogen or
oxy-acetylene flames.

The most notable features of atomic-hydrogen welding
are the entire absence of oxidation on the one hand, and of
carburisation on the other.   Ordinary carbon steels are in
fact decarburised at the weld when this method is used, and
this effect may limit the application of the method to such
steels.   Decarburisation of high chromium steels, however,
takes place much less readily but, if it should occur, it would
be a distinct advantage for many purposes for which such
steels are welded.

Freedom from oxidation effects may be noted in Fig. 225,
representing a section through a weld between two sheets of
20 per cent. chromium stainless iron.   A strip cut from the
sheet was used as filler rod and the weld was made without
the least trouble.   The fact that high chromium irons can
be welded without difficulty, using filler rods of similar
material, is a distinct advantage as such a procedure would
be difficult, to say the least, if the oxy-acetylene blow pipe
were used.

All types of stainless steels may be electrically welded by
*spot, seam or butt methods.   Spot welding is frequently used
for many domestic articles made from stainless steels ;   the*
structural characteristics of a spot weld between two stainless
iron sheets are shown in Fig. 226, representing a section
through the weld.   Lap and seam welding of thin sheets
have also been used for the manufacture of containers of
various types, e.g. for chemical and domestic uses.

Butt welding may be conducted on the usual machines
employed for ordinary steels.   If stainless steel has to be so
welded to ordinary steel, it is necessary, owing to the higher

Plate L
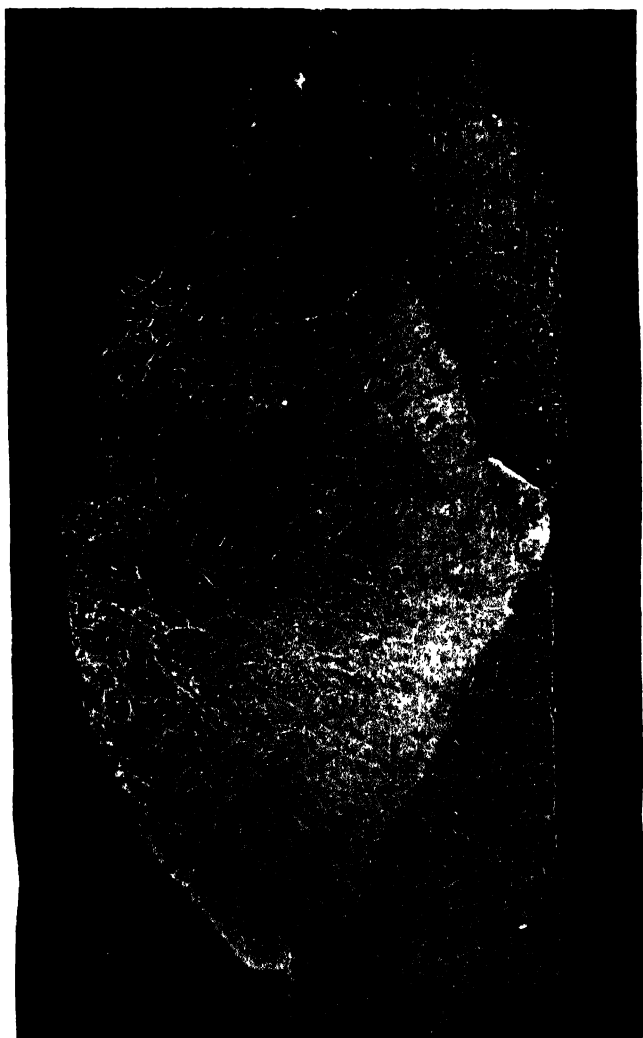
Fig. 225.—Section through weld made by Atomic Hydrogen process in stainless iron containing 0.12 per cent. carbon and 20.9 per cent. chromium, using filler rod of same material.

12

electrical resistance of the former, to have the ordinary steel projecting further out of the contact grips than the stainless steel.

Special types of machines are not necessary in arc welding ; those normally used for mild steel are satisfactory. Special electrodes, however, must be used,* otherwise the joint would not be corrosion resisting.   When melted down, the electrodes should produce an alloy of approximately the same composition as the stainless material to be welded. For this purpose the electrode should consist either of—

(1) a core of the required stainless alloy surrounded by a wrapping of asbestos cord (to act as a flux), held in position by a binder with which is mixed a reducing agent such as ferromanganese, aluminium or calcium silicide ; or

(2) layers of metals which will melt down to give the required composition, together with flux and reducing agent as above.

The latter type of electrode is known as a " Synthetic " electrode and its " make up " will depend on the kind of steel being welded.   Thus for a straight chromium steel, an electrode may consist of—

(a) an iron or mild steel rod ;

(b) a wrapping of asbestos cord ;

(c) a binder, plus powdered ferrochrome and a deoxidiser.

An electrode suitable for an austenitic chromium-nickel steel may be given its necessary nickel content in the form of an electro-deposited layer of nickel on the iron or mild steel rod, but would otherwise be similar to the one described above. In some cases, the deoxidiser consists of a fine aluminium wire wound on the rod before the asbestos cord.

During the melting down of an electrode, loss of chromium occurs owing to oxidation.   The electrode should preferably contain 3 or 4 per cent. more chromium than is required in the weld.   The amount lost actually depends on the skill of the welder and the care he exercises ; if the welding is carelessly done, i.e. if too long an arc is used, the figure may easily exceed 3 or 4 per cent.

* Suitable electrodes are made, e.g. by Messrs. Murex Welding Processes, Ltd., Walthamstow, and by Messrs. Welding Rods Ltd., Atterclffe Road, Sheffield.

When ordinary carbon steels are welded to austenitic stainless steels, there is always a thin hard band formed on the carbon steel side of the joint.   In all probability, this is caused by the diffusion of chromium and nickel into the carbon steel, producing at some point a composition which is inherently martensitic.   The presence of this band need not occasion any trouble unless the welded joint is bent in such a way as to cause fracture to run along it.   A similar band is produced when straight chromium steels are welded to ordinary steels using the oxy-acetylene process and a welding rod of austenitic chromium-nickel steel.

Turning now to the effects of the welding operation on the properties of the steel at and adjacent to the weld, it is obvious that these should be considered in the light of the probable structural changes which will occur in the various steels when these are locally heated up to their melting points and cooled rapidly therefrom ; the former produces a coarse structure in the parts so heated while the rapid cooling may, or may not, induce hardness, depending on composition.   The austenitic steels may be considered first as they are the simplest.   Judged solely from a mechanical standpoint, properly made welds in these steels would be perfectly satisfactory without any further treatment because the steels do not harden at all as a result of rapid cooling from any temperature : also, it is one of their outstanding features that they retain their ductility and toughness even when made very coarsely grained.   The welded tube shown in Fig. 224, for example, had not been heat treated in any way before it was bent to the shape shown.   From a corrosion resistance point of view, however, treatment is generally essential in order to avoid the intergranular breakdown which has been described in Chapter V, page 276. Obviously a welded article must be heat treated as a whole ; a local heat treatment would merely transfer the weakened area to some other place.

The effects of welding on non-austenitic steels may be considered along with the typical curves in Fig. 227, which give the hardness values of five representative types of steel after quenching from the temperatures indicated.   Materials of the kind represented by curves A and B are not so often welded as the milder varieties. The most notable feature with these steels is the production at, and on each side of, the

• *Plate LI*

Fig. 226. Section through spot weld between two stainless-iron sheets (10 gauge). 15. The position of the weld is evident from the unwelded area of the sheets which are visible on either side of the photograph.

weld, of a very hard band, which is liable to crack.   As a precaution, the weld should be tempered as soon as possible after the welding operation is completed : the joint need not become quite cold before this is done ;· as soon as it has cooled sufficiently to become strongly magnetic, it may be immediately heated to the tempering heat, e.g., by a " soft " torch.
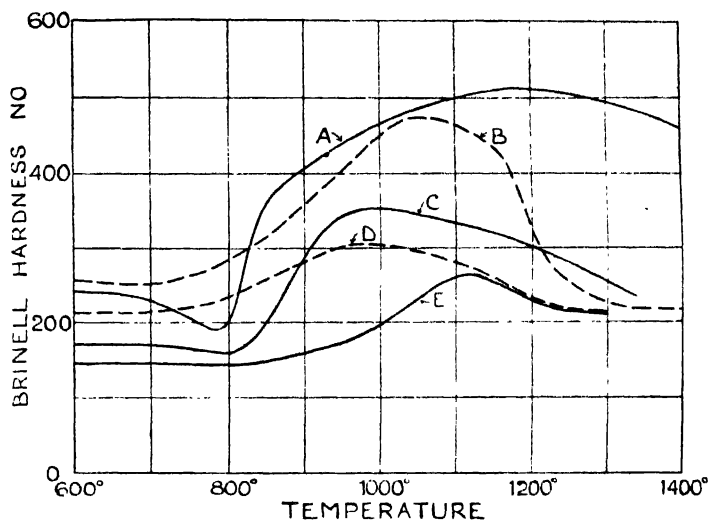
Fig. 227.   Hardness values of typical irons and steels after quenching from the temperatures indcated.

Curve	Carbon %	Chromium %	Nickel %
A	0·3	14·0	0·3
B	0·23	18·0	2·4
C	0·08	14·0	0·3
D	0·09	18·1	2·2
E	0·13	17·2	0·14

Stainless iron, such as is indicated by curve C (Fig. 227) and the mild " Twoscore " type of steel, curve D, do not harden nearly so much on cooling from high temperatures and hence are more suitable for welding operations.   Welds made in such steels should however be tempered in order that their toughness and ductility may be increased, although it is possible to obtain welded joints in stainless iron sheet which will bend through 180° satisfactorily without any subsequent heat treatment.   Again, the tempering need only be a purely local treatment ; it can be done by going over the

joint, immediately it has cooled sufficiently to become strongly magnetic, with a soft torch, so as to heat it to 650°/700° C.

Tempering, however, does not refine the coarse structure inevitably produced at a welded joint and which, in all these non-austenitic steels, entails a distinct loss of ductility in the material. This coarse structure may, however, be removed to a considerable extent in these four types of materials by hardening and tempering the welded article instead of merely tempering it; the mechanical properties of the joint are thereby noticeably improved. Such a procedure may not always be necessary but may be usefully applied to welded joints which are likely to be subjected to considerable stress when in use. For example, in the production of seaplanes, a steel similar to D, Fig. 227, is frequently used for welded joints where a high degree of strength, together with considerable toughness and ductility are required; in such cases, the complete welded articles are air-hardened from 950° C. and then tempered so as to give the required tensile strength.

The high chromium irons, typified by curve E in Fig. 227, harden to a small extent only but they are distinctly less ductile than usual after being air cooled from high temperatures; welded joints in these irons should therefore be heated to 700°/750° C. These irons become very coarse grained after heating to temperatures above about 1,050° or 1,100° C., and this coarse structure cannot be removed by any form of heat treatment. Hence, welded joints in these high chromium irons are never very tough or ductile; generally speaking, they are only suitable for lightly stressed parts, e.g., ornamental work.

Pickling. The pickling of stainless steel can be carried out quite successfully if certain precautions are observed. If the steel is pickled in the ordinary sulphuric or hydrochloric acid baths it will be found that there is a tendency for the scale to come off in patches only and that if the articles are left in the bath for a longer time in order to remove the rest of the scale, the acid attacks the steel in the places where the scale has already come off, pitting it badly, while the scale remaining on is hardly affected. This is particularly liable to occur if the scale is fairly thick. This undesirable state of affairs, however, can be avoided if a small

amount of colloidal organic matter, such as one of the " Restrainers " on the market, is added to the bath. With such an addition, the ordinary pickling bath containing about 5 to 10 per cent. of sulphuric acid acts very well.* The surface produced by such a pickling bath has a tendency to be rather dull in appearance ; it may be brightened up considerably by placing the pickled article for a short period in a cold bath containing about 5 per cent. nitric acid. This bath has little or no action on the steel but it has the effect of improving considerably the appearance of the pickled article. Alternatively a hot solution containing 10/30 per cent. nitric acid may be used for brightening the surface ; this solution acts more quickly than the cold dilute one but is more troublesome to use.

Pickling baths containing hydrochloric acid are also frequently recommended for stainless steels as having a more rapid action than sulphuric acid. Strengths of 20/50 per cent. of the commercial acid, to be used at a temperature of 50°/60° C., are generally specified. In some cases, a higher temperature, 70°/90° C. is suggested for the austenitic steels. Alternatively, a 10 per cent. solution of sulphuric acid, to which 6/12 per cent. (by weight) of rock salt has been added, may be used ; such a bath is claimed to work faster than the ordinary sulphuric acid solution. All material pickled in this solution or in the hydrochloric acid baths should subsequently be given the nitric acid dip.

Where a very good surface after pickling is desirable, use may be made of a pickling bath containing 3 to 5 per cent. nitric acid and 1 per cent. of hydrochloric acid. This bath should be used cold ; it works rather slowly but produces a silvery grey surface. The time required varies, with the thickness of the scale, from about half-an-hour or an hour for a very thin coating to about 24 hours for a thick scale. This bath will probably be most useful where thin scale, such as is produced by tempering, has to be removed ; for example, in making pressings of stainless iron it may be necessary to do the cold work in several stages and

* A suitable restrainer may be made by mixing one part of glue size with one part of concentrated sulphuric acid and then immediately adding, with constant stirring, two parts of water. The mixture, of course, becomes hot (which, it may be remarked, facilitates the reaction between the acid and the glue size), and is ready for use as soon as cold. With a bath containing 5 per cent. sulphuric acid and used at a temperature of 60° to 70° C, the restrainer may be added in the proportion of 1 part to 100 parts of the bath.

to soften the material between these. For the softening operation, reheating to 700°/750° C. is all that is necessary. Such a reheating produces only a thin film on the surface ; this film can be quickly removed by the special pickling bath leaving a bright silvery surface in perfect condition for further pressing.

The austenitic chromium-nickel steels may be given a particularly pleasing surface by the use of a suitably restrained, hot solution of hydrochloric and nitric acids A suitable mixture is :—

Commercial hydrochloric acid (conc.)	25% by volume.
„ nitric acid (conc.) ...	5% „ „
Restrainer	½% „ „

The restrainers sold under the trade names* " Rodine," " Galvene " and " Pickelette " have been found satisfactory. The best results are obtained when the temperature of the bath is about 60°/70° C. There is a distinct attack on the steel when this bath is used ; this should be allowed for when, for example, sheets of a specified thickness are being produced. Sheets and plates should always be placed on edge in the bath ; if laid flat, the under side will probably be patchy in appearance. Articles of complex shape should be kept on the move. The time required depends on the thickness of the scale, but the minimum is about 20 minutes. If the bath conditions are properly adjusted, the material becomes passive towards the end of the pickling period, so that action practically ceases and the article leaves the bath with a very pleasing bright surface.

Two or three precautions are necessary. The bath must be kept oxidised by adding small quantities of nitric acid from time to time as required. Should the acid strength become considerably reduced, either by dilution or as a result of attack on the steel, pitting of the latter is almost certain to occur. If the bath is heated by blowing steam through it—a method very commonly employed for heating pickling baths—dilution is inevitable ; for this reason, it has been found desirable, in works practice, where such heating methods are employed, to commence with a bath containing about 50 per cent. hydrochloric acid and continue

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* These three are obtainable respectively from Sir W. S. Royce & Co., Ltd., Albert Square, Manchester; Messrs. British Dyestuffs Corp., Ltd., Manchester, and Messrs. Ferguson, Wild & Co., Middlesborough.

using it until the acid content falls to too low a figure.   The bath may be regenerated by the further addition of hydrochloric acid, as well as the periodical doses of nitric acid mentioned above, and this may be continued until, owing to the presence of large quantities of dissolved salts, it no longer produces a satisfactory surface.

When starting to use a new bath, or on restarting an old one after standing for some time, it is always advisable to pickle a few scrap pieces of material first, to make certain that the bath is in proper working order.

Probably the most perfect surface, e.g. on a sheet, is produced by removing the scale by means of the ordinary sulphuric acid bath, described earlier, and then using the nitro-hydrochloric acid bath merely to obtain the peculiarly bright surface which is its special feature.   This procedure also has the advantage that the special bath remains in a cleaner condition, owing to the absence of scale.   The bright pickled surface is particularly adapted for articles which are not intended to be polished subsequently; the surface it gives is very pleasing and especially suitable for articles for domestic use or for decorative work.   On the other hand, sheets which are to be polished after the pickling operation are best treated in the ordinary sulphuric acid bath first described ;   the surface thus obtained, though matt, is flatter, i.e., more free from depressions, and therefore more readily polished than that of the " bright pickled " article.

It should be emphasised that this particular bath is only suited to the austenitic chromium-nickel steels and perhaps a few of the more complex alloys formed from these.   It is not recommended for the hardenable chromium steels or the stainless irons, nor is it possible to obtain with these materials the characteristic bright pickled surface which is produced on the austenitic steels.

It may also be noted that austenitic steels which have been wrongly treated and, as a result, contain a network of free carbide do not give the characteristic bright surface when pickled in this bath.   If a welded article, which has not been subsequently heat treated, be pickled, a band on each side of the weld will remain dull.

Scale may also be removed from stainless steels by electrolytic means.   The article to be descaled is made the anode in a bath, which is not necessarily of an acid nature.

Thus T. Rondelli patented* a process of this type in which a bath containing 15 per cent. or more of caustic alkali is employed at a temperature of about 140° F.   The article to be descaled is made the anode and a current density of 4 or 5 amperes per square decimetre is recommended.   The scale is converted into soluble iron compounds which are then removed by immersing the articles in a weak acid bath, hydrochloric and sulphuric acids being recommended ; the acid bath in removing the loosened and altered scale, gives the article a bright surface.   The use of an alkaline bath for electrolytic pickling is not, however, essential; acid solutions may be employed with perfect success and have advantages in some cases.

The surfaces produced by electrolytic pickling are generally very good ; they are free from pits or other depressions such as are occasionally produced in ordinary acid pickling, even when carefully performed, and they are therefore very suitable for polishing.   The method appears to be particularly valuable for the stainless irons and hardenable stainless steels of higher chromium content as these are always more difficult to deal with, than the lower chromium alloys, in the ordinary acid pickling bath.

Unless there is some special reason to the contrary, stainless steel should not be pickled when in the hardened condition.   Hardened material is generally in a greater or less state of internal stress, and if pickled in such a condition, is liable to develop surface cracks.

Heat Treatment of Stainless Material.   The subject of the heat treatment of stainless steels of all types is large and many-sided, particularly if the effects of variations in composition and temperature of treatment on the physical properties obtained be taken into account.   In the present chapter it is intended to deal only in a general manner with the subject, as a detailed consideration of factors such as those mentioned above has already been given.   It will simplify matters if stainless irons and the hardenable stainless steels (i.e. those of groups (1) and (2), page 470) are considered first, and afterwards the austenitic types.

Unless the special precautions mentioned earlier in this chapter are fully carried out, the hardenable stainless steels of group (1), which have been forged or rolled at the

* British Patent No. 228,278. (Nov. 6th, 1923.)

ordinary temperatures for such operations, are more or less hard when cold and therefore require to be softened before any machining or chipping operations can be carried out. The treatment for such a softening process is very simple ; the material merely requires to be reheated to the maximum tempering temperature available for the particular steel, and allowed to cool in air, or if preferred it may be quenched in oil or water. In the case of the plain chromium steels, this temperature is 700°/750° C., but the presence of any considerable amount of nickel (e.g., 1 or 2 per cent.) limits the maximum temperature available to 700° C. or even 650° C. After this operation, the material will have a Brinell hardness number of about 150 to 270 (corresponding to a tensile strength of 35 to 60 tons per square inch), depending on its composition, and in this condition it machines easily. The operation is simply that of tempering the steel at the highest possible temperature consistent with commercial conditions. A still greater degree of softness, more particularly with the higher carbon varieties, can be obtained by annealing the material, though in this condition, like all annealed steel, it does not machine so smoothly as in the hardened and tempered condition, but is much more liable to tear.

For the annealing process, for reasons which will be evident from Chapter II (page 46), the steel should be heated to 50° or so above the Ac.1 change point (i.e., to 850°/880° C. in the case of the plain chromium steels) and, after allowing to become evenly heated, should be either cooled slowly through the Ar.1 change (e.g., down to 600° C.) or else transferred to a second furnace kept at 600° to 700° C. and, after becoming even, should be held for a sufficiently long period at this temperature to enable the carbon change to take place completely, as described earlier in this chapter. In this case as full annealing, i.e., the production of very soft material rather than the prevention of cracking is the object in view, the soaking time should be generous ; unless the steel is abnormal in composition (e.g., contains considerably more nickel than usual) a soaking period of one or two hours should be ample, after which the material may be air cooled or quenched. For the same reason, if the material is slowly cooled in the furnace, the rate of cooling from about 750° to 600° C. should not be faster than 50°

an hour.   If the steel does not contain any large amount of nickel, or other metal which lowers the temperature of the Ar.1 change, there is no need to continue the slow cooling below 600° C.   By such annealing processes, the Brinell hardness number of 12/14 per cent. chromium 'steel, containing 0·30 to 0·40 per cent. carbon, may be reduced to between 170 and 200.

Sometimes a greater degree of softness than is obtained by tempering forged or rolled material, as described on page 497 is desirable and, at the same time, annealing may be inconvenient or impracticable, e.g., in the case of steels which, on account of rather high nickel content, require holding for a very prolonged period at the temperature at which Ar.1 occurs in order that this change may take place completely. On such occasions, the hardness of the tempered article may be reduced if, prior to tempering, it is heated to a temperature about 30 or 50 degrees above the Ac.1 point and air cooled therefrom.   As will be evident from Figs. 81 and 86, the material hardens after such a treatment but not to the same extent as when air cooled from forging heats ; hence, having a lower initial hardness when so treated, it is softer after tempering.   The added softness produced in this

TABLE CXXXV.

Softening of Rolled or Forged Material.
(See above.)

Mark.	Carbon %	Chromium %	Nickel %	Brinell as Rolled.
A.	0·22	13·0	0·60	555
B.	0·23	17·5	2·42	444

Mark.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hardness Number.	Izod Impact, ft. lbs.
A.	T. 700° C.	47·0	53·8	21·0	54·6	255	53
	A.C. 850° C., T. 700° C.	23·0	45·7	27·5	63·6	269/212	66
B.	T. 650° C.	53·1	64·6	14·0	83·5	311	13
	A.C. 800° C., T. 650° C.	43·3	55·9	22·0	51·0	311/262	48

manner is evident in the results given in Table CXXXV. Obviously, the articles may be cooled more or less slowly in a furnace, instead of more rapidly in the air, from the intermediate low hardening heat, with sometimes an added gain in softness.

All material, whether it has been tempered or fully annealed for machining or other purposes or is still in the more or less hardened condition as result of the forging or rolling operations, requires final heat treatment in order to give the best combination of strength, ductility and toughness for the purpose in view and incidentally to develop its greatest degree of resistance to corrosion.

To harden such steel, it should be heated to a temperature which is, in general, in the range 900°/950° C., and then be cooled in air or quenched in oil or water, depending on circumstances. If the cross section of the piece is reasonably small and only a moderate degree of hardness is required, air cooling is generally satisfactory. When a greater degree of hardness is required or if the cross section of the piece is large, then oil quenching may be used. Water quenching is permissible if the section is symmetrical and able to withstand great stresses, or if practicable and convenient as in the case, for example, of knife blades. The hardening capacity of stainless iron depends on its chromium content. Material with about 10 to 14 per cent. chromium and 0·07 to 0·10 per cent. carbon will oil harden, or air harden in reasonably small sections, from a temperature of 950° C., to a Brinell hardness number of 250 to 350. With a higher content of chromium than this, however, the hardening capacity falls off considerably (as indicated in Fig. 84, page 59), so that at about 16 per cent. chromium one cannot obtain a Brinell hardness of more than about 250, even by water quenching small samples, while the maximum hardness obtainable by air cooling is less than this.

Where articles of complex shape have to be dealt with, especially if the carbon content is fairly high, air cooling is preferable to oil quenching, in order to minimise hardening stresses. If, at the same time, the cross section of the article is fairly great in parts, so that the rate of cooling of such parts is hardly fast enough to harden them sufficiently, advantage may be taken of the fact that the capacity of the steel for air hardening increases as the hardening temperature rises. For

such purposes a temperature of 950° to 975° C. may be used or even 1,000° C. It is not advisable to exceed the latter temperature, however, as by so doing a coarse structure is liable to be produced. Where such difficulties arise in the production of sufficient hardness by air cooling, and oil quenching is not advisable, matters may be helped considerably by using a steel containing one per cent. or thereabouts of nickel, because the presence of this element greatly retards the rate at which the critical changes take place on cooling and hence allows the material to harden at slower rates of cooling (see page 139).

As a general rule, the tempering operation should follow the hardening as soon as possible, in order that stresses set up in hardening may be relieved before they have an opportunity to cause cracking. This, of course, applies equally to all steels which harden intensively. There is no need to wait until the article is quite cold after hardening. The lowered change point which results in the production of martensite from austenite generally takes place between about 150° C. and 400° C. (see pages 93 and 472) depending on composition and hardening temperature and as soon as this change has taken place completely, the article may be reheated for tempering. As the steel becomes strongly magnetic when the above change takes place, a magnet may be used as a guide.*

Articles which are to be retained in the hard condition should preferably be tempered between 200° and 400° C. after hardening. By so doing, quenching stresses are relieved and the toughness improved distinctly. It has been shown earlier (Fig. 13) that such tempering has practically no effect on hardness. Owing to this resistance to tempering, it is possible, in the case of the plain chromium steels, to combine the hardening and tempering operations by quenching the material from the hardening temperature in a fused salt or metal bath, the temperature of which is kept between 150° and 250° C. Such a method is valuable for articles which are liable to crack when quenched in the ordinary way. It is important to note that the temperature of the bath should not be allowed to rise above the range indicated above. The upper limit is fixed by the fact that the temperature must be lower than that of the

* See p. 475 with respect to stainless iron, however.

lowered change point, otherwise the material is retained in the austenitic condition whilst in the bath, and fully hardens on cooling from the latter. Obviously also, the method cannot be used for those hardenable steels in which the lowered change point is likely to occur below 250° C., e.g., those containing two per cent. or so of nickel.

Some little difficulty may be experienced in properly refining 12/14 per cent. chromium steel which has been badly overheated, especially if, after such overheating, it has been allowed to cool slowly, producing a pearlite structure. This is especially the case if the carbon exceeds about 0·3 per cent. The cause of this will be evident from the description of the microstructure given in Chapter II. Material which has been slowly cooled from a high temperature consists of pearlite and frequently, as shown in Fig. 8, the distribution of the carbide in such pearlite is by no means uniform, even when the steel is of eutectoid composition. In steel of lower carbon than this, the distribution of carbide is still more irregular owing to the presence of ferrite (see Figs. 3 and 21). When such material is reheated to 900°/950° C. for hardening, the ground mass of austenite formed at Ac.1 is, of course, refined, but the carbide which remains undissolved at these temperatures (see Figs. 10 and 23) still outlines the original coarse structure and hence the material, after such hardening, is not properly refined. In the case of steels containing more than 0·3 per cent. carbon (i.e., hyper-eutectoid) the excess carbide which has probably formed a network round the grains of the overheated material, as in Fig. 4, remains quite undissolved at 900°/950° C., and further aggravates matters. Such cases are dealt with by reheating material containing 0·3 per cent. carbon or less to 975°/1,000° C., or in the case of higher carbon steel, to a temperature sufficiently high to dissolve the excess carbide (see Fig. 27), and air cooling therefrom, so as to keep the carbide evenly diffused. The articles may then be hardened and tempered in the normal way.

Hardening from such high temperatures as those given above for the preliminary heat treatment is rather prone to lead to cracking, especially if the article has a form. which is likely of itself to cause trouble in this respect ; it may therefore be necessary to take precautions to avoid this. Such cracking almost invariably occurs either while

the article is passing through the lowered change point or afterwards. Where cracking is liable to occur, therefore, the article should be air cooled down to about 450° or 400° C. (in order to prevent the separation of pearlite or troosite at Ar.1) and may then be cooled comparatively slowly through the range in which the lowered transformation occurs. Thus, after it has cooled down to about 400° C., it may be charged into a furnace at this temperature and allowed to cool slowly in that, or the cooling rate may be retarded by other means such as packing in hot ashes. As in the normal hardening operation, the article may be reheated for the final hardening process as soon as it has passed through the lowered change point and before it becomes cold.

The improvement which is brought about by such a preliminary treatment as that given above may be illustrated by the following tests obtained on two bars ($1\frac{1}{8}$ inches diameter) of steel of the following composition :—

Carbon	...	...	0·30%
Silicon	...	...	0·17%
Manganese	...	...	0·23%
Chromium	...	...	12·4 %
Nickel...	...	...	0·55%

These bars were heated for 3 to 4 hours at 1,100° C. and then slowly cooled, so as to produce a very coarse pearlitic structure. After this treatment they had a Brinell hardness number of 202 and an Izod impact figure of 5 ft. lbs., the fracture being coarsely crystalline. Bar A was given a refining treatment at 1,000° C. and was then hardened at 900° C. and tempered at 700° C. in the usual way. Bar B was hardened at 900° C. and tempered at 700° C., along with A, but was not given the refining treatment. These bars gave the following tests :—

	Yield Point, tons per square Inch.	Maximum Stress, tons per square Inch.	Elongation per cent. on 2 inches.	Reduction of Area per cent.	Izod Impact. Ft. Lbs.
A. (refined)	38·2	52·6	25·0	58·2	59 64
B. (not ,,)	36·8	49·8	22·0	48·5	26 24

The improvement in the microstructure brought about by this refining treatment is typified by a comparison of Fig. 15 with Figs. 9 and 10. The structure of the refined bar was similar to Fig. 15 ; in the unrefined piece, the plates of the carbide formed a " ghost image " of the original structure, resulting from the annealing operation, in a fashion typified by Figs. 9 and 10. Such plates provide a favourable path on which a crack may readily travel. On the other hand, the structure shown in Fig. 15 is free from all traces of this coarse structure.

The treatment of the austenitic steels does not present any great difficulty except such as arises from the fact that they require heating to relatively high temperatures in order to soften them completely. They are of course not liable to hardening cracks or any other such troubles experienced with hardenable steels. The only heat treatments which should be applied to austenitic steels are of two types :—

(1) That intended to produce the softened form of the material and consisting of heating to, followed by cooling rapidly from, a sufficiently high temperature to produce a structure consisting solely of austenite and free from the network of carbide obtained by reheating to lower temperatures. The minimum temperatures required depends on the composition of the steel and varies generally between 1,000° and 1,200° C.

(2) That occasionally applied to cold worked material and consisting of reheating to a low temperature, certainly not more than 500° C. Such a treatment is akin to that used for " blueing " cold drawn wire or cold rolled strip of ordinary steel. While such a treatment as this is possible, it is not generally very effective in its results, as will be evident from the data given in Figs. 117 and 118.

No austenitic steel should be reheated in the range 500°/900° C. as a final treatment nor should it be slowly cooled in this range from a higher temperature. Treatments of these descriptions result in the formation of carbide films round the grain boundaries with consequent liability for intergranular attack. If material has been treated in this manner during manufacture or fabrication into some article, it should be given, whenever possible, a final heat treatment of

type (1) above. ᶵ This point is particularly important in material intended ϡor use in the chemical industry.   As has been seen in the preceding pages of this chapter, the fabrication of vessels by boilermakers' methods sometimes leads to plates being heated to temperatures of 700°/900° C. or so, or being locally heated to these or higher temperatures.   Local heating always occurs when vessels are welded.   All these conditions entail a greater or less area of the plate or vessel being heated in the range 500°/900° C.   While this may be immaterial in a few cases, e.g., spot-welded domestic ware, it would have disastrous results in the majority of purposes for which the materials are used.   Whenever such heating has occurred in plates or vessels intended for chemical purposes, the plate or vessel should be given, if it is at all possible, a final heat treatment of type (1) above.   Herein lies one of the difficulties attending the use of welded vessels of austenitic steels ; the final heat treatment must then be carried out after the welding is completed, an operation attended with considerable difficulty in the case of large vessels or intricate systems of welded pipes.   In those cases where heat treatment is possible (and it is obvious that where large scale plant is involved the operation may be impossible owing to lack of a furnace of sufficient size) considerable ingenuity is frequently required in ensuring that the treated vessel or other part does not deform under its own weight while heated to the requisite high temperature.

Cold Working.   Stainless steels may be cold worked in much the same way as ordinary steels ; thus they may be drawn into wire, rolled into sheets or strip, made into weldless drawn tubes or pressed or stamped into a variety of shapes. The power required for these various operations depends on the initial hardness of the steel and the rate at which it hardens as a result of cold work ; it is generally greater than in the case of mild steel.   The extent to which the metal can be deformed at one operation varies with the· kind of stainless steel used. Generally speaking, stainless irons and the austenitic steels are selected for cold working operations owing to their greater softness and ductility as compared with other types of stainless steels ; and of these two varieties, stainless irons are more easily worked and deformed than the austenitic steels.

Possibly the greatest difficulty in drawing operations,

either for the production of wire or of special sections such as turbine blading, lies in the tendency of the steel and the die to seize, causing scoring of the drawn material. The best remedy is proper choice of lubricant, and for this hard soap or mixtures of tallow and soft soap have been used successfully.

Stainless steels cannot be " coppered " with the solutions used for this purpose with ordinary steel as these have no action on the stainless steel. A film of copper may, however, be deposited on the steel electrolytically.

For the production of good wire, it is essential that the hot rolled rod be carefully pickled. The pits in an over-pickled surface are not taken out in drawing ; on the contrary, they are more or less closed up and remain as fine seams in the finished wire.

When producing high tensile wire in steels of the harden-able type, it is advisable to obtain part of the hardness by an initial heat treatment rather than to depend on the heavy drawing of very soft rods. Some results on previously hardened and tempered rods, after drawing various amounts have been given in a previous chapter ; see page 130.

The pressing and deep drawing of sheet or strip presents no great difficulty. Stainless irons or the austenitic chromium nickel steels are the most suitable ; in the latter case, especi-ally, more power is required than for similar work on ordinary mild steel. Generally speaking, a rather greater clearance between punch and die than is usual with mild steel should be adopted for the stainless materials, particularly the austenitic varieties, and a reduction in pressing speed is advisable. Owing to their high rate of work hardening, the austenitic steels are much more severe on the press tools than the stainless irons. The blades of shears must be very well adjusted and be sharp, particularly with the austenitic steels, or the metal will not cut cleanly.

During punching operations on plate, sheet or strip, the austenitic steels, being very tough and ductile, do not fracture after the hole has been partly cut, as occurs with ordinary carbon steel. The metal must be cut completely through. Hence, the punch and die must fit more closely than is customary when punching mild steel. Also, as a result of its rate of work hardening and its toughness, it is not gen-erally possible to punch a hole, in an austenitic steel sheet, of smaller diameter than the thickness of the sheet.

Both the stainless irons and the austenitic steels may be formed by spinning, though the operation is sometimes troublesome with the austenitic steels on account of the rapidity with which they harden.

All lubricant should be removed from the surfaces of cold worked articles before they are annealed. If this is not done, distinct surface carburisation may readily occur during the annealing operation, leading to hardness and loss of ductility and also reduction in corrosion resistance. It cannot be too strongly emphasised that high chromium steels readily absorb carbon at high temperatures and that the rate of absorption is particularly fast in the case of the austenitic steels owing to the high temperature required for their heat treatment.

As regards intermediate annealings or softenings, the following treatments are suitable :—

(a) for irons and steels containing 12/14 per cent. chromium and for high chromium irons (e.g., 16 per cent. or over) heat to 700°/750° C. and cool rapidly or slowly as may be convenient ;

(b) for steels containing 16/20 per cent. chromium and about 2 per cent. nickel, heat to 625°/675° C. cooling rapidly or slowly ;

(c) for austenitic steels, heat to 1,000° C. or over, depending on composition and cool rapidly.

It was mentioned in Chapter IV that the austenitic steels could be partially softened, after cold work, by heating them to 800° or 900° C., but that such softening was likely to reduce the ductility of the steel ; see pages 188 and 189. It is also very likely to cause considerable trouble if the steel so softened be pickled before proceeding with the next cold working operation. Material softened at these temperatures will contain free carbide at the grain boundaries, leading to intergranular attack during pickling. If this occurs slightly, the surface of the steel may be badly roughened but a bad attack on thin material would probably lead to the latter disintegrating entirely.

Abnormal grain growth may easily occur on annealing high chromium irons which have been submitted to critical amounts of cold deformation. Houdremont,* for example,

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* "Die Rostfreien Stahle, ihre Eigenschaften und Herstellung." Dr. Ing. E. Houdremont. Kruppsche Monatshefte. Nov 1930.

Plate LII

2%   4%   7½%   14%   25%.
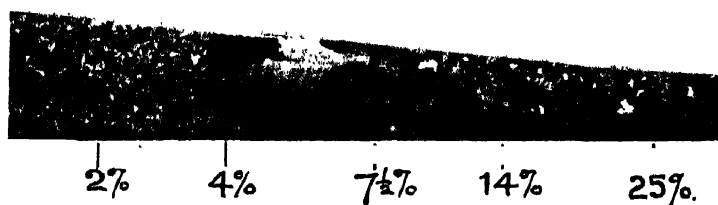
Fig 229   Grain growth in cold worked " Anka " steel after reheating to 1,250° C   The sample was in the form of a conical test piece which had been stretched to the amounts indicated on the photograph.

To face page 507.]

showed that a stainless iron containing about 16 per cent. chromium became exceedingly coarse grained when annealed at 800° C. after 8 to 10 per cent. deformation, and when annealed at 900°/1,000° C. after 2 to 10 per cent. deformation. Annealing at 1,050°/1,100° C. after similar amounts of deformation produced a considerably finer structure. His recrystallisation diagram for this steel is reproduced in Fig. 228. In the case of material containing about 0·3 per cent. carbon and 25/30 per cent. chromium, similar abnormal grain growth was produced in material which had been deformed between 2 and 5 per cent., by annealing at all temperatures between 700° and 1,100° C. but particularly at 900°/1,000° C.
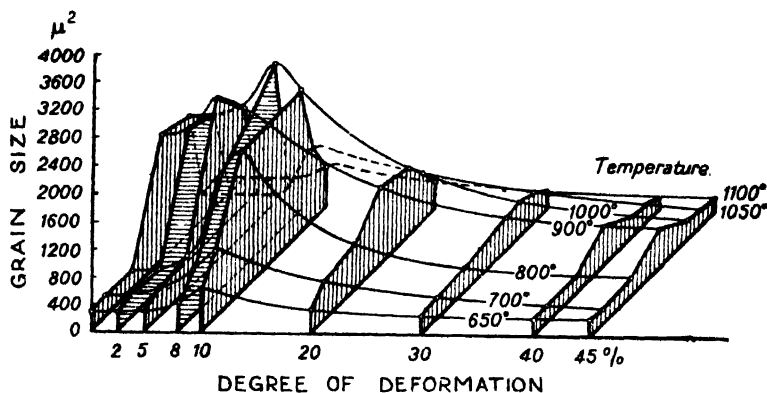
Fig. 228. Effect of degree of deformation and reheating temperature on the grain size of 16 per cent. chromium stainless iron. (Houdremont.)

A similar abnormal grain growth, though probably not to such an excessive extent, may be produced in the austenitic steels if they are softened at temperatures of about 1,200° C. and over after being deformed about five per cent. Fig. 229 for example, shows the grain size of a conical test piece which was stretched in a testing machine and then softened at 1,250° C. The figures on the diagram indicate the percentage reduction in cross sectional area during stretching. No such grain growth was produced when material similarly deformed was softened at 1,100° C.

Machining. If comparisons as to machining ability are to be made with mild steel or brass, it is well to state at once that all stainless steels are more difficult to machine than these

metals.   Most engineering shops, however, have experience
of harder steels than mild steel ; high tensile alloy steels are
regularly dealt with and, if these be taken as standard, the
comparison is not so one-sided.   Broadly speaking, it may
be said that the hardenable stainless steels and the stainless
irons machine with the same ease as carbon or alloy steels of
the same tensile strengths.

The austenitic steels may cause considerably more
trouble if certain precautions are not observed.   These latter
are necessary solely on account of the rapid rate at which
these steels harden when cold worked.   A tool should never
be allowed to rub over the surface to be cut or the latter may
harden so much as to become almost unmachinable.   Tools
must be kept sharp and they must be made to cut all the time
they are at work.   Wherever possible, a cut once started
should be completed without check of any kind, due either
to the tool coming in and out of cut or to the stoppage of the
machine in the middle of a cut.   Centre-punching for
drilling should be very lightly done and the drill, once started
in a hole, should be pushed through with a continuous feed.
It should not be allowed to revolve idly without cutting or
the further drilling of the hole may be impracticable.

Drilling is in fact one of the most difficult operations
with the austenitic steels because there must always be a
small area at the point of the drill, between the flutes, which
does not cut.   The work hardening of this central area does
not prevent a drill of large diameter from cutting, because a
sufficiently heavy pressure may be maintained on it, but in
the case of drills of small diameter, the trouble becomes acute ;
it is practically impossible to drill holes 1/32 inch diameter,
or less, of any depth in the austenitic steels.   In order to
minimise the trouble, twist drills of high speed steel should
always be used ; the included angle between the cutting
edges should preferably be ground to 115° as against the
standard 118°, and the drill point thinned.   The cutting
lips of the drill should be ground with more clearance than
standard ; 16° is satisfactory.   The short spiral flute drill
used for drilling copper and aluminium, if ground as above,
gives good results.

It is desirable that the drills used should be as short as
possible and, when a drill chuck is used, the drill should be
gripped for as long a length as possible in the chuck so as to

reduce any spring to a minimum. All these recommendations aim at securing that the drill should be held as rigidly as possible; obviously the drilling machine itself should be above suspicion in this respect; for example, the drill spindle should be free from play.

TABLE CXXXVI.

Drilling Speeds and Feeds for Stainless Steels.

Size of drill, ins.	Hardenable Steels, (50/60 ton).		Austenitic Steels.	
	Revs. per minute.	Feed per rev.; ins.	Revs. per minute.	Feed per rev.; ins.
$\frac{1}{8}$	1,200	0·004	800	0·003
$\frac{1}{4}$	600	0·006	500	0·005
$\frac{3}{8}$	400	0·008	300	0·007
$\frac{1}{2}$	300	0·010	220	0·008
$\frac{5}{8}$	250	0·011	180	0·009
$\frac{3}{4}$	200	0·012	160	0·010
$\frac{7}{8}$	180	0·013	150	0·011
1	160	0·014	130	0·012

Particulars as regards drilling speeds and feeds are given in Table CXXXVI; where stainless irons are concerned, the speeds given for hardenable steels may be increased 10 per cent.

TABLE CXXXVII.

Tapping of Austenitic Steels.

Tap size.		Drill size.	
$\frac{1}{4}''$	Whitworth	$\frac{13}{64}''$	diameter
$\frac{3}{8}''$	,,	$\frac{5}{16}''$	,,
$\frac{1}{2}''$	,,	$\frac{27}{64}''$	,,
$\frac{5}{8}''$	,,	$\frac{35}{64}''$	,,
$\frac{3}{4}''$	,,	$\frac{21}{32}''$	,,
$\frac{7}{8}''$	,,	$\frac{49}{64}''$	,,
$1''$	,,	$\frac{7}{8}''$	,,

Tapping holes is another fruitful cause of trouble with austenitic steels. The chips can never escape freely from a

tap and, by the nature of the tool, a great deal of rubbing occurs.   The drilled hole should be made slightly over-size if it is to be successfully tapped ; Table CXXXVII gives dimensions which have been found successful in practice.

For hand tapping, four-fluted ground-thread taps give the best results ; a little tallow on the tap is helpful. Machine tapping may be done, on the austenitic steels, at about 10 or 12 feet per minute when it is possible to employ a tap with a long lead.   Machine tapping on blind holes is not satisfactory.

Generally speaking, the hardenable stainless steels do not give very good results when machine tapped.

It will be gathered that comparatively little trouble is likely to occur in lathe work.   Apart from the necessity of continuous cutting in the case of the austenitic steels, the most important requirement is rigidity.   It is wise to have the tool supported as near the cutting point as possible and it is also advisable to increase the top rake of the tool some 2° to 5° above the standard used on ordinary " 40-ton " steels.

There are some other considerations, however, which are worthy of attention.   The degree of corrosion resistance of stainless steels in general is lessened by distortion, hence it is desirable that machined surfaces of these steels should be as little distorted as possible.   All machining leaves the machined surface in a more or less distorted condition but the latter is greatest when the cuts are heavy and least when they are fine.   It is also greater when the cutting edge is blunt and less when this edge is sharp.   It follows therefore, that distortion is likely to be least when fine cuts are taken with sharp tools and, if these conditions are adhered to, high speeds may be used.   These ideas are followed out in the data given in Table CXXXVIII ; it should be understood, of course, that conditions will vary with length of bar and rigidity of tool and machine.   Experience has shown that surfaces prepared in this way need little grinding preparatory to polishing ; and it may be mentioned, in amplification of this Table, that if it is impossible, for any reason, to finish an object by grinding, it may be turned with very fine cuts at feeds of about 120/160 per inch and speeds of 80/100 feet per minute.   The subsequent mirror polishing of such a machined surface is easily achieved by file and emery cloth.

TABLE CXXXVIII.

Turning Speeds and Feeds for Stainless Steels.

Size of bar.	Depth of cut; ins.	Stainless Irons (35/45 ton).		Hardenable Stainless Steels (50/60 ton).		Austenitic Steels	
		Feed per rev.; ins.	Speed; ft. per min.	Feed per rev.; ins.	Speed; ft. per min.	Feed per rev.; ins.	Speed; ft per min
Up to 1″ diam.	$\frac{1}{32}$	0·03	60	0·03	55	0·03	50
	$\frac{1}{16}$	0·025	55	0·025	50	0·025	45
	$\frac{1}{8}$	0·02	50	0·02	45	0·02	40
1⅛″ to 2″ diam.	$\frac{1}{32}$	0·04	60	0·04	55	0·04	50
	$\frac{1}{16}$	0·03	55	0·03	50	0·03	45
	$\frac{1}{8}$	0·03	50	0·03	45	0·03	40
2⅛″ to 3″ diam.	$\frac{1}{32}$	0·05	60	0·05	55	0·05	50
	$\frac{1}{16}$	0·04	55	0·04	50	0·04	45
	$\frac{3}{32}$	0·03	50	0·03	45	0·03	40
	$\frac{1}{8}$	0·03	45	0·03	40	0·03	40
3⅛″ to 4″ diam.	$\frac{1}{32}$	0·06	60	0·06	55	0·06	50
	$\frac{1}{16}$	0·05	55	0·05	50	0·05	45
	$\frac{3}{32}$	0·05	50	0·05	45	0·05	40
	$\frac{1}{8}$	0·05	45	0·05	40	0·05	40

NOTE. To get maximum production, adhere to the speeds and feeds given above and increase the depth of cut as much as the work will allow. In some cases, it may be advisable to reduce the feed slightly and increase the depth of cut.

Brazing and Soldering. There is no particular difficulty with regard to the soldering of any type of stainless steel. Ordinary lead-tin solder does not unite with stainless steel quite so easily as it does with ordinary steel (the austenitic steels are somewhat better in this respect than the chromium irons and steels) but there is no difficulty in making a joint. Zinc chloride is a suitable flux though some of the proprietary articles on the market, e.g., "Soldo," can be used with success.* It is important that the surfaces of the stainless steel be well cleaned before the operation and all traces of the flux must subsequently be carefully removed, by washing, from the completed joint otherwise corrosion may occur.

If there is any difficulty in making the solder adhere to

* A saturated solution of zinc chloride in a mixture of equal parts of concentrated hydrochloric acid and water also acts very well.

a polished surface of the steel, the latter may be dulled by etching.   A suitable etching solution contains :—

Hydrochloric acid ... 90 parts by weight.
Ferric chloride   ... 50   „   „
Nitric acid   ... 3   „   „

The solution should be allowed to act for 5 or 10 minutes and then wiped off.

Stainless steels may be brazed, though with some little difficulty, with the ordinary copper-zinc brazing mixtures, using borax as a flux.   As in soldering, the surfaces must be perfectly clean and they should be protected by the borax while being heated.   A much greater difficulty than is concerned with the operation itself arises, however, with the condition that stainless steel assumes as a result of the heating to which it has to be subjected for the brazing operation.   The ordinary copper-zinc brazing mixture (60 per cent. copper, 40 per cent. zinc) requires the material which is to be brazed to be heated to a temperature of 950° C. or higher for the process to be successful.   If, as is generally the case, the heating is purely local, the results would as a rule be very undesirable, from a corrosion resistance point of view, in the case of austenitic steels ; hence brazing is not generally to be recommended for such steels.   The structural changes produced in the steel are precisely similar to those already described under welding ; but in this case, a subsequent heat treatment operation is impossible as it would melt the joint.   If, however, the articles to be brazed were small, so that they could be wholly heated to 950° C. or over and then cooled rapidly when the brazing operation was completed, the process would be feasible.

Stainless irons and steels, other than those of the austenitic variety, if heated in a similar manner, harden to a greater or less extent on cooling from the brazing heat.   Hence, when a brazed joint is made in such material, the parts of the latter immediately surrounding the joint will be more or less hard and brittle when cold.   This condition can of course be rectified by tempering the brazed joint at 600°/700° C., but this is not always convenient or even possible.   For example, the blades of a turbine are frequently brazed to lacing wires which hold them firmly together, preventing an undue amount of flexure.   It is generally not feasible to temper the

whole of such a disc, after the lacing wires have been brazed into position, owing to its size and for other reasons. In order, therefore, to minimise the production of hard brittle spots in such blades it is preferable to use a brazing mixture having a considerably lower melting point than the ordinary 60 : 40 brass. It has been found that an alloy having the following composition :—

Copper	...	...	44 per cent.
Zinc	...	...	33 ,,
Silver	...	...	23 ,,

is very suitable for this purpose. It melts at a temperature of about 700° C. and hence allows the brazing to be carried out with much less danger of hard brittle spots being formed in the stainless material afterwards. It also forms a very strong joint.

It is also obvious that for purposes involving brazing, it is preferable to use the lower carbon stainless iron than material of higher carbon content, because the former air hardens to a very much less degree than the latter, especially from temperatures not much higher than the Ac.1 point. By using the lower carbon material, the bad effects of an accidental overheating in the brazing operation are very much less marked than they are with the higher carbon steel.

Using the brazing mixture mentioned above, pieces of stainless iron strip, 2 in. wide, $\frac{1}{16}$ in. thick, have been brazed and then, without further treatment, the strip bent through 180° close to the joint without the latter showing any sign of failure or the strip in the neighbourhood showing the least sign of cracking.

When colour in the brazed joint is of importance, e.g., in the brazing of silver or silver plated handles on to stainless steel blades of table knives, the following mixture has been found suitable :—

Copper	...	...	27 per cent.
Zinc	...	...	11 ,,
Silver	...	...	62 ..

Soldering and brazing have only a limited use in connection with stainless steels. Neither process should as a rule be used for the manufacture of chemical equipment, not only because the solder or brazing metal is likely to be less

resistant to many chemicals than the steel, but also because the presence of dissimilar metals in contact in such plant is likely to cause electrochemical action. Generally speaking, when a fusion joint is essential, autogenous welding is preferable to either brazing or soldering. Soldering, however, is frequently a useful method of making joints in dairy equipment where it is essential that the joint should possess a perfectly smooth surface; the solder should of course have a sufficiently high content of tin to be unacted upon by the dairy produce. Brazing is widely used at present by turbine manufacturers as a means of fastening blades in position and of attaching lacing wires and shrouding rings to the blades. These seem to be the main uses of these two processes.

SELECTION OF STEELS FOR INDUSTRIAL PURPOSES

Stainless Steels were discovered rather less than twenty years ago ; the data given in the preceding pages suggests that already the material included in this category covers a wide range of products, differing materially in chemical composition and mechanical properties. The complexity of the subject has already aroused comment among engineers, who have asked why there are so many kinds of corrosion-resisting steels and how is a would-be user to select from the numerous varieties one to satisfy his own particular requirements.

There are good reasons for much of this seeming complexity. In the first place, the engineering profession, from long usage of ordinary steel, has come to regard this metal as one possessing a very wide range of hardness values. It is desirable, therefore, that stainless steel be producible in forms equally soft or hard, as the case may be, so that any stainless steel part may have mechanical properties similar to those which experience has shown to be most suitable in the ordinary steel article it replaced.

Secondly, it was found that stainless steels were not resistant to any and every form of corrosive attack. The continually widening sphere of their applications revealed weaknesses in their chemical stability, and continuous endeavours have been, and are being, made to produce new varieties of the steel which will give satisfaction where previously failure has resulted.

But it may be asked, why not discard the older, less resistant types, and concentrate on the manufacture of the newer, more resistant alloys ? The avoidance of unnecessary multiplication of products by the standardisation of one or two types would lead to cheaper and more economical manufacture. This has already been done to a considerable extent, but there are at least two good reasons why a variety of types should still be manufactured, the possible economies of further standardisation notwithstanding. In the first

place, some of the modern complex alloys are much more expensive than their simpler prototypes, and it is not economical to use a very expensive alloy when one considerably cheaper will give perfect satisfaction. The advantages of using alloy steels for many purposes are realised by the engineering world but the widespread use of these steels has not made ordinary carbon steels obsolete, nor is it likely to do so. The former are employed when their special properties can be used to advantage.

Similarly, if one of the simpler types of stainless steel resists perfectly satisfactorily the attack of steam, for example, it is not necessary or even desirable to cease its use for this purpose because it is not equally stable against the action of boiling acetic acid, or some other very corrosive chemical. Secondly, the question of mechanical properties is often of equal importance to corrosion resistance and in regard to the former properties, some of the simpler types of stainless steel have great advantages, in that they respond well to heat treatment operations ; generally the complex forms do not. Under mechanical properties, must also be considered ease of fabrication by ordinary workshop processes and this frequently exerts a notable influence on the selection of steels for various purposes.

Commercially, however, the subject is not so complex as would appear. Experience, and the necessity for as great a measure of standardisation as is practicable, has led to the use of half a dozen types of the steel whose salient features may be summarised as follows :—

(1) Stainless irons and steels containing 12/14 per cent. chromium : a family of steels, which, of all those classed under the term stainless, most readily approaches ordinary carbon steel in the extent to which mechanical properties can be influenced by heat treatment processes and by variation in carbon content. This group may be regarded as a series of high tensile steels possessing great corrosion resistance.

(2) Stainless irons containing 16/20 per cent. chromium. These are soft alloys which, in general, are brittle under impact and are not amenable to heat treatment operations. An exception in this respect is the special " Brearley ' K ' " brand of Messrs. Brown, Bayley's Steel Works, Ltd., which possesses a considerable measure of toughness.

Steels containing about•25 or 30 per cent. chromium together with not more than about 0·5 per cent. carbon may also be included in this group.   These steels have mechanical properties very similar to.those of the 16/20 per cent. chromium irons except that they are somewhat harder and less ductile than the latter.   They are mainly used for heat resisting purposes.

(3) Low carbon steels containing 16/20 per cent. chromium, which possess the capacity of being hardened and tempered, due to a small content of nickel.   The mechanical properties of these steels are influenced by heat treatment and by variation in carbon content in a similar manner to those of group (1) though the available range of hardness values is more restricted than in the latter.

(4) Austenitic chromium-nickel steels of which the Krupp " V.2.A." is the prototype ; these are the most generally used of the austenitic steels.   They may only be hardened by cold work and the effectiveness of heat treatment operations is confined to the removal of cold working effects and the production of certain structural characteristics necessary from the point of view of stability against corrosive attack.

(5) Steels of group(4)whose resistance to certain severely corrosive chemicals has been increased by the addition of such metals as copper, molybdenum, silicon, tungsten.

(6) Austenitic steels of high nickel content whose main features are great strength and resistance to oxidation at high temperatures ; their chromium content may vary considerably, depending on the service required of them, and additions of other metals, e.g., tungsten and silicon are occasionally made in order further to enhance their special properties.

In this guise, the apparent complexity of the situation is reduced considerably, and particularly if it be understood that those steels classed in groups (5) and (6) are to be regarded as special purpose materials with, as yet, a limited application.   The other four groups are necessary as regular products to meet the varied requirements of the engineer. There is an old German proverb to the effect that trees do not grow up to heaven ; in its implication of lack of perfection, the proverb is particularly true of steels in general and stainless steels in particular.   The early corrosion resisting steels of

group (1) were found to be lacking in the degree of their corrosion resistance. Efforts to improve them in this respect were successful but led at the same time to the partial or complete loss of the characteristic feature of response to hardening and tempering operations which these steels possessed in common with ordinary carbon steels. As a result, the selection of a suitable stainless steel for a particular purpose from among the six groups listed above involves frequently a compromise between the conflicting requirements of corrosion resistance, mechanical properties and ease of fabrication into various forms.

The first commercial use of stainless steel was for the manufacture of cutlery and by now the composition of material for this purpose has become practically standardised; about 12/14 per cent. chromium and 0·3 per cent. carbon is the rule* though, as has been noted in a previous chapter, less chromium than this suffices to produce a knife which will retain its polish perfectly under ordinary domestic use.

For the manufacture of table or kitchen ware—forks, spoons, dishes, saucepans and such like articles—soft material capable of being cold worked easily is required. Either stainless irons (preferably containing not less than about 14 per cent. chromium), or the austenitic chromium nickel steels of group (4) are suitable. The former are more easy to fabricate in some cases, but the latter have generally a rather more pleasing colour when polished.

From its initial use for table cutlery, obvious steps led to the adoption of stainless steel for other kinds of knives (e.g., pocket knives, and those of a more or less technical application) and for scissors and surgical instruments. Surgical knives are made of steel similar to that used for cutlery ; for instruments possessing no cutting edge but requiring a certain degree of springiness (e.g., forceps of various kinds) a steel of lower carbon content—0·15 per cent. or so—is suitable.

The use of the austenitic steels for parts of dentures seems to have advanced to a considerable extent in Germany, largely owing to the efforts of the famous Essen firm. Steel of this type would appear very suitable for this purpose from the standpoint of both strength and corrosion resistance. Probably the greater difficulty in working it as compared with

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* Higher contents of carbon (0·6 per cent) and chromium (16/18 per cent.) appear to be used to some extent in America. It is difficult to see what possible advantage such a steel can have over the standard form used in this country.

the non-ferrous alloys generally used, particularly in regard to the making of hard soldered joints, has been largely responsible for the slowness of its adoption by the dental profession in countries outside Germany.

No great strength is generally required of ornamental fittings, and hence one can use for their manufacture the very high chromium irons, e.g., 17 to 20 per cent. chromium, which are distinctly more resistant to general corrosion than those of lower chromium content, but are usually not nearly so tough as the latter.   Alternatively, one may employ the austenitic steels; these are, indeed, superior to the irons if castings are necessary, and they are also generally preferable for outdoor use in urban districts owing to their greater resistance to sulphuric and sulphurous acids, small amounts of which are likely to be present in the atmospheres of such places.

The use of stainless steels, and particularly the austenitic varieties, for household fittings, especially for bath rooms, has attained considerable proportions.   Rather more recent is its more general application in architectural work.   The bright surface of the steel, when either polished or suitably descaled, lends itself for decorative effects and one may note its increasing use for both indoor and outdoor fittings for shops and other large business establishments.   A number of shop fronts, erected recently both in London and the provinces, have embodied stainless steel fittings.   The façade of the Savoy Hotel in London will be familiar to many, but perhaps the most striking example of its use for this purpose is found in the Chrysler Building in New York; the whole of the tower surmounting this building is encased in sheets of austenitic steel containing about 18 per cent. chromium and 8 per cent. nickel.   Many of the internal metal fittings, e.g., for windows and doors, are also made of the steel, some 500 tons of which were used in the construction of the building.

Owing to its high reflecting power when polished, and also the permanence of such a surface, stainless steel is an ideal material for reflectors for flood and other lighting purposes.   At the present time, a prominent feature of the London skyline is a tower on which letters constituting the name of a well-known food product are fashioned in polished stainless steel sheets and are illuminated at night time by hidden flood lights.

The last few years have provided an equally notable, though quite different, architectural use of stainless steel, namely for the preservation of old and valuable buildings. The renovation of St. Paul's Cathedral has attracted considerable attention and it may be interesting if some technical considerations underlying the selection of suitable steels for this purpose are briefly considered. As the work was intended to be as permanent as the wit of man could make it, the most resistant steels were necessary. The choice lay between the hardenable high chromium steels of the " Twoscore " type and the austenitic chromium-nickel steels. The former possess the high yield point and other mechanical properties of a hardened and tempered steel ; the latter are characterised by a very low yield point. Hence where ability to withstand high stresses without permanent deformation was essential, the hardenable steel had obvious advantages.

Probably the dome of the cathedral caused the greatest anxiety. The fabric consists here of a triple dome supported by a double drum of masonry, surrounded by an open colonnade visible from the street, the whole being finally supported from the foundations on eight massive piers. The latter are eccentrically loaded and were constructed of very poor material. The defective material has been reinforced by pumping concrete grout into the interior of the piers and by inserting massive tie bars of stainless steels, but the eccentric loading of the piers has a tendency to push them out of the vertical and allow the drum to spread in diameter. This tendency is accentuated by seasonal variations in temperature ; the drum expands in hot weather but, owing to the poor tensile strength of masonry, does not contract by an equal amount when the temperature falls.

To stop the progressive spreading of the drum with the attendant evils in the supporting piers, two stainless steel chains have been constructed and fitted. The first chain encircles the outer drum wall of the dome structure at a point just below the Whispering Gallery. It comprises an articulated chain of the pin and link type, built up of three full links alternating with two full and two half links, the section of a full link being three and three-eighth inches square. The total length of this chain is about four hundred and fifty feet and it weighs about thirty-five tons. The second chain forms a thirty-two sided polygon and is fitted round the

bases of the thirty-two bastions to the outer wall of the drum at the level of the clerestory walk. This chain is also of the pin and link type, the links being of similar design to those in the first chain, and is considerably longer than the latter. At eight points, tie rod attachments are fitted for tangent anchorages into the four large bastions at the base of the drum.

These claims are designed to withstand a load of a thousand tons which, it is anticipated, will be sufficient to prevent any further increase in drum diameter. It may be noted that each chain has an effective cross-sectional area of some thirty-four and a quarter square inches; at maximum load, therefore, the intensity of the stress in the steel is approximately twenty-nine tons per square inch, a figure made possible by the use of a hardenable steel.*
Obviously the chains must not deform plastically under the stress imposed upon them or they will no longer give the necessary support to the masonry. Had the austenitic type of steel been used, it would have been necessary to limit the stress intensity to about one-third of the value adopted, with the result that chains three times as heavy would have been required, an obviously undesirable addition both to the weight to be supported by the piers and to the cost of the steel reinforcement.

In other parts of the reinforcement, e.g., tie rods embedded in masonry, where ability to withstand high stresses without plastic deformation was not so essential or where a lower ratio of strength to weight could be adopted, the austenitic steels were no longer unsuitable on mechanical grounds and considerable quantities of these steels were effectively used in this manner.

Equally with the architectural world, the motor industry is now turning its attention to the merits of corrosion resistant steels. At least one well-known make of car is being entirely equipped with polished metal fittings of stainless steel. Probably the claims of the steel in this respect have been overshadowed during the last two or three years by chromium plating, but the advantages of using a material which does not depend for its surface stability on the adhesion of a thin metallic coating are being realised. Many metal fittings for

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* The properties specified were : minimum proof stress, 30 tons per sq. in. ; tensile strength, 45/50 tons per sq. in.

cars are pressed from sheet ;' for these, capacity for deep drawing and ability to take and retain a highly polished surface are the main desiderata. Other fittings are most easily produced as castings. In both cases, the austenitic steels provide suitable material, though considerable quantities of high-chromium iron sheet and strip have been used for pressings.

The desire to extract the last ounce of power from a petrol engine has necessitated increased attention being paid to the materials of which the engine is built, in order that they may have adequate strength for the demands made upon them under service conditions. Many interesting comparisons could be drawn in this respect between the materials used twenty years or so ago and at the present time for similar parts ; and none more interesting than with regard to valves.

Modern conditions in a petrol engine necessitates its valves, and particularly its exhaust valves, being heated to relatively high temperatures, and they must function properly while so heated.

This problem first assumed considerable importance during the war, owing to the rapid development of powerful engines for aircraft. It was soon found that stainless steel had useful properties as a valve material and large quantities were so used during the war. Indeed, the manufacture of valves was the second major commercial use of stainless steel. Since that time the valves of engines used for other purposes than aircraft have been fabricated from various heat resisting steels, more or less allied to the " stainless " family.

The properties desirable in a valve steel were summed up very concisely by Aitchison.* Apart from such important features as ease of forging, of heat treatment and of machining, which concern the production of a valve rather than its performance, a valve steel should possess the following properties :—

(1) The greatest possible strength at high temperatures.

(2) The highest possible impact value.

(3) The least possible tendency to scale, and if scaling does occur, the scale should be as adherent as possible.

* " Valve Steels for Internal Combustion Engines." Proc. Inst. Auto. Eng. Vol. XIV (1919), p. 31.

(4) The ability to retain its original physical properties after repeated heatings to high temperatures followed by cooling to atmospheric temperature, also after being heated to an elevated temperature for a considerable period of time.

(5) No liability to harden when cooled in air from the temperature it will attain when used normally as a valve in an engine.

(6) Sufficient hardness to withstand excessive wear in the stem.

(7) The capacity of being hardened at the foot of the stem with considerable ease if necessary.

The list is very comprehensive and some of the desired properties are rather conflicting.

Inlet valves give the least trouble; in many cases, carbon steels are used and if a tougher product seems desirable, 3 per cent. nickel steel serves very well. A similar steel but containing in addition up to about 1 per cent. chromium is frequently suggested but it has the disadvantage that if it should reach a temperature of about 700° C. or over in service, it is liable to harden on subsequent cooling; it is also more susceptible than the nickel steel to temper brittleness induced by prolonged heating between about 400° and 550° C.

None of these steels, however, possesses any great strength at temperatures above about 600° C. and exhaust valves frequently become hotter than this. To meet these more severe working conditions, several types of " stainless " steels have been used, the most important having the compositions indicated below :—

Mark.	Carbon ·%	Silicon %	Chromium %	Nickel %	Tungsten %	Cobalt %
A.	0·3/0·4	—	12	—	—	—
B.	0·4/0·6	0·7/1·2	6·0/8·0	—	—	—
C.	0·4/0·6	2·5/3·0	6·0/8·0	—	—	—
D.	1·5	—	12/14	—	—	3·0/3·5
E.	0·4/0·5	1·5/2·0	12/16	10/12	2·5	—
F.	0·3/0·5	2·5/3·0	16/18	25	—	—

Material A corresponds to the ordinary ": cutlery" quality stainless steel and was the first steel of the stainless family to be used for valves. Experience indicated, on the one hand, that the carbon content could be raised to some extent with advantage and, on the other hand, that so much chromium was not essential, particularly if silicon were present to the extent of 1 per cent. or so, as in steel B. These two steels, A and B, are suitable if the valve does not reach in service a higher temperature than about 800° C. If raised above this temperature, they are liable to harden on cooling. A greater addition of silicon, as in steel C, raises the hardening temperature to about 950° C. This steel has also considerable strength at temperatures up to 700°/800° C. but above this, it rapidly becomes softer as was shown in an earlier chapter (see page 447). The cobalt chromium steel D has been used to some extent but it is expensive and it seems doubtful whether its properties at high temperatures are worth this high cost.*

Austenitic steels, such as E and F, are considerably stronger at temperatures above about 700° C. than any of the previous steels; in addition they have no tendency to air harden after being heated to any temperature. They have been widely used for exhaust valves working under very severe conditions. They are expensive but have been found to justify their cost.

Summing up, it may be said that valve conditions may be classified broadly into four groups :—

(1) Valves (generally inlet valves) whose working temperature is less than about 600° C. Carbon steels or 3 per cent. nickel steels often meet these conditions satisfactorily.

(2) Valves which may reach a temperature not higher than about 800° C. Steels A and B are suitable, the latter being somewhat cheaper and also somewhat stronger at working temperatures.

(3) Valves working under very severe conditions, i.e., whose working temperature exceeds about 800° C. or where very great strength while hot is desirable. Austenitic steels such as E and F should be used in these cases.

(4) An intermediate set of conditions which are satisfied

* Aitchison (*loc. cit.*) concluded that they were not.

by steel C; these are mainly where resistance to scaling and freedom from airhardening effects at temperatures up to about 950° C. are necessary but where it is possible to design the valve so that the stresses set up under working conditions are within the capacity of this steel.

The ability of stainless steels to resist corrosion and erosion makes them extremely suitable for many parts in connection with steam and hydraulic service. It may be useful to deal briefly with the selection of suitable steels, and their heat treatment, for these purposes.

It is generally assumed by engineers that leakage past steam valves is caused mainly by foreign matter being trapped between the valve and valve seat. Their faces become indented and the slight leakage which is thereby produced rapidly becomes serious owing to the erosive action of the steam escaping via the damaged portion of the seat or valve face. A hardenable form of stainless steel may be made much harder than most other valve metals and is less likely than the latter to be damaged by trapped foreign matter. Moreover, should it be so damaged, it will be less eroded—if at all—by the escaping steam. Experience extending over several years has shown that steel containing 12/14 per cent. chromium and 0·2/0·3 per cent. carbon is particularly suitable for steam valves. Both valve and seat may be given a Brinell hardness value of 370/400, a suitable treatment being airhardening from 950° C. followed by tempering at about 300° C. to relieve hardening stresses. Parts to be so treated should be machined to size (plus grinding allowance where necessary) before treatment ; afterwards they should be pickled and then machine-ground on the working faces. Alternatively, for ease of fabrication, the valve seat may be tempered at about 600° C. after hardening, so as to give a Brinell hardness value of about 270 ; it may then be machined after heat treatment. If this course is adopted, the valve should be so designed that the harder valve face overlaps that of the softer seating ; by this arrangement, cutting and grooving of both faces, owing to pressure between the two, is avoided.

As indicating the type of service obtainable from stainless steel steam valves, it may be mentioned that a safety valve of the " Ross " type, made of this steel, was tested on a locomotive of the Great Northern Railway of Ireland ; the

railway company reported that after two years' service at a working pressure of 175 pounds per square inch, it was as good as new, whereas bronze valves never lasted more than two months. Stainless steel safety valves fitted to shunting locomotives in daily use at Messrs. Brown, Bayley's Steel Works, Ltd., have been in service over five years and have not once required " grinding-in " ; steam stop valves for injectors and steam jets on the same locomotives are still tight after three to five years' service. The steam pressure on these locomotives is 140 pounds per square inch.

If wet steam is being dealt with or if condensation may occur frequently or over fairly long periods, it is preferable to use the higher chromium steels of the " Twoscore " type so as to avoid the chance of electro-chemical attack occurring due to contact with copper alloys. " Twoscore " steel is thus preferable for injector cones, feed check valves, blow off cocks and water gauge fittings. This steel should be heat treated so as to possess hardness values similar to those recommended for the lower chromium steel. Steel of this type (or alternatively an austenitic steel of the " V.2.A." class) should also be used for the spindles of steam stop valves ; greater freedom in the choice of packing material is thereby possible ; see pages 325 *et seq. re* contact corrosion.

In passing, the results of tests on different packing materials may be cited as evidence of the superior resistance to wear of stainless steels. For these tests, which extended over a period of three years, two similar " Weir " pumps were employed ; in one of the pumps, carbon steel was used for the steam piston rod and, in the other, stainless steel ; similar packing being fitted in both cases. The tests were primarily carried out for the purpose of noting the relative wear of the two steels, the tests on various packings being a secondary consideration, but they showed that the type of packing used was of considerable importance, inasmuch as it influenced not only the amount of wear of the rods but also the relative efficiency of the stainless steel.

When a greasy graphited asbestos packing was used, the amount of wear of the carbon steel was five times that of the stainless steel ; on substituting a rubber asbestos packing, the ratio rose to 56 to 1 whereas when use was made of a packing composed of rubber, asbestos and white metal and having a wearing face consisting largely of the last named, the

ratio was 8 to 1. The actual amount of wear of the stainless steel during similar periods was about the same with all the packings, the loss in diameter being about 0.0005 inches in all cases. The carbon steel, on the other hand, was extremely sensitive to the type of packing used, the amount of wear of these rods during similar periods varying between 0·025 and 0·0140 inches.

A word as to details of construction may not be out of place here. If a cast iron or cast steel valve body be employed, the stainless steel seating may be simply pressed into position. Should the body be of a copper alloy such as bronze, however, it is necessary to screw in the seating or else make a rigid attachment by means of bolts, otherwise, owing to the coefficient of expansion of stainless steel being much less than that of bronze, the seat would become loose when hot and lift with the valve, making the latter inoperative. For the same reason, stainless steel plugs fitted in gunmetal or bronze bodies must be given an ample taper : at least 1 in 2½ if the cock is intended for hot work. A smaller taper will result in the plug binding in the body when the two cool down. The gunmetal body of such a cock may be expected to fail sooner or later by erosion, necessitating regrinding ; for this reason a harder alloy, e.g., of nickel-copper, would be more suitable for the body. It is undesirable to use stainless steel for both plug and body owing to the probability of seizing occurring.

Should " grinding-in " be necessary in a stainless steel valve, the faces of the valve and seating should be smeared with a small amount of fine carborundum paste and the two then lightly ground together by hand. Only the lightest pressure should be exerted and after two or three turns the faces should be cleaned. If these precautions are taken, the operation is simple and sure, but if too much pressure is exerted or the faces are not regularly cleaned, the metal is likely to seize and tear, giving a rough surface difficult to deal with.

It is well known that when two pieces of ordinary steel are rubbed together under pressure there is a distinct tendency for the surfaces to seize. The tendency is still greater in the case of stainless steels and, if ignored, may lead to considerable trouble. The surfaces of screw threads in stainless steels must always be finished very smoothly and

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nuts should fit easily on the bolts on which they are to work, otherwise seizing may occur when the nut is being run down. For the same reason, if stainless steel discs and seats are used in valves of the parallel flow type, the faces will probably score due to seizing. The tendency for this to occur may be reduced by making both disc and seat as hard as possible (e.g., with a Brinell hardness value of 400/450) but generally speaking it is advisable in valves of this type to make the seating of a hardenable stainless steel and the disc of a good nickel-copper alloy ; e.g., one containing about 55 per cent. nickel and 35 per cent. copper, the remainder consisting of small amounts of tin, iron, zinc, etc. There is no tendency for such a combination to seize. In valves of this type, erosive attack is more severe on the seating than on the disc, the latter being out of the path of the steam when the valve is fully open ; hence the more resistant metal, stainless steel, should be used for the seating and the softer nickel-copper alloy for the disc, rather than vice versa.

The benefits resulting from an intelligent use of stainless steel parts are equally evident in hydraulic work. Actually this was recognised some years before the use of the steel for steam valves was thought of, a result probably due to the fact that steel works are amongst the largest users of hydraulic power and were thus likely to suffer from the failure of the metals, previously obtainable, to stand up to the severe demands made upon them. It is a fact that either late in 1913 or early in 1914, three large stainless steel rams were fitted to a forging press pump in a Sheffield works and to-day, seventeen years or so later, they are still in service.

Mild steel rams and spindles deteriorate in more ways than one. Corrosion proceeds continually though it is not always visible ; reciprocating rams, for example, appear bright while at work because the packing continually wipes off the rust which is formed. The latter, however, embeds itself in the packing where it acts as an abrasive, scoring the surface of the rod. Leakage through the packing results and this is corrected by tightening up the latter, thus accelerating the abrasion and scoring of the rod. In addition to the cost of renewing parts thus worn, the delays due to stoppages for adjusting packings amount in the aggregate to a serious loss.

Bronze is sometimes used as a substitute for mild steel ;

but although it is less likely to suffer corrosion, it is easily scored or abraded owing to its softness and it has a relatively low crushing strength. Hence it is seldom satisfactory with high pressures.

On the other hand, stainless steel is not only much more resistant to corrosion than bronze or mild steel but it can be made much harder than either ; hence it is less easily abraded or scored by packings or eroded by water containing solid particles in suspension. In order to develop these properties to the greatest degree, pump rams or plungers of stainless steel should preferably be rough machined and then hardened (e.g., at 950° C.), followed by tempering at about 800° C. to remove hardening stresses. If screwing or further machining is required at one or both ends, the ram or plunger should be locally tempered at about 650° C. at these parts. The body of the ram or plunger, being hard, should be ground to size. Prepared in this manner, it will have, under ordinary working conditions, a life far in excess of that to be expected from the use of any other known metal.

Experience over a number of years has shown that the use of stainless steel for pump rods, piston rods, rams, as well as for valve parts and similar purposes, has led to considerable economies due not only to the longer life of the respective parts but also to increased life of packings, reduced number of stoppages for repairs —and therefore increased output from plant—reduction of losses through leakage and lower frictional losses of rams and piston rods. As giving some indication of the relative wear of bronze and stainless steel, the following example of two hydraulic pump rams working under identical conditions may be quoted. The rams were 1·5 inches diameter ; after one month's service, one of them, made of bronze, had been reduced 0·014 inches by wear. The other ram, of stainless steel, wore only 0·005 inches in nine months. The pressure in each case was two tons per square inch and " Talcrom·" packing was used.

In another case, a 3¼ in. ram of stainless steel worked for two and a half years with water at a pressure of 850 lbs. per square inch and was then reduced in diameter by 0·005 inch only ; at the same time the average life of the leather " U " packings was nine months. The abnormally

long life of " U " leather packing, when used with stainless steel rams, is one of the most outstanding features of the use of this material and leads to very considerable economies in the upkeep of hydraulic appliances. That lessened wear on the leathers would be found is understandable, because the hard stainless steel ram takes a high polish and retains this polish in use ; owing to its hardness it is not easily scored. The actual increase in life of the leathers is, however, considerably greater than would have been anticipated.

Economies arising from the use of stainless steel in steam and hydraulic plant, and due to reduction in loss of time due to stoppages, are very considerable and in general far exceed the initial cost of the stainless steel part. The following example is typical of many others which have been brought to the author's notice. During the war period, a phosphor bronze valve in connection with a 1,200-ton forging press was constantly giving trouble. It required " grinding-in " every three weeks and although this was done regularly, troubles leading to stoppages were of frequent occurrence. At this period, stoppages were particularly obnoxious and moreover very costly ; in this case it was estimated that the loss due to stoppage was of the order of £1 per minute. A stainless steel valve was fitted ; during the next two years the valve never required " grinding-in " and no stoppages due to valve trouble occurred.

Stainless steel has also been effectively used for parts of water turbines, particularly for needle valves. The latter, when made of other metals, suffer severely from erosion, especially if the water contains solid impurities, and, as irregularities in the surface of the valve have an adverse effect on the steadiness of the jet and the efficiency of the turbine, the matter is of considerable importance. Stainless steel needle valves retain their original smooth surface after long periods of service, and the absence of friction and the complete regularity of the jet enable the efficiency of the machine to be maintained at a high figure.

Generally speaking, the type of stainless steel most useful for hydraulic plant is that containing 16/20 per cent. chromium together with sufficient nickel (about 2 per cent.) to make it hardenable. The 12/14 per cent. chromium steel is suitable in some cases but the greater resistance of the higher chromium material against electrochemical attack,

due to contact with copper alloys or with graphite, and against contact corrosion generally (see page 325) makes its use desirable. The austenitic steels of the " V.2.A." family are also equally satisfactory on these grounds but they are not so resistant against erosion and abrasion.

For parts required in the cast form, e.g., impellors and Pelton wheel buckets, the austenitic steels are preferable owing to the greater ease with which they may be obtained in the form of satisfactory castings.

One of the most important engineering applications of stainless steel is for turbine blading. The modern tendency for the use of higher temperatures and pressures in steam plant has made very severe demands on the materials used for its construction ; and particularly does this apply to turbine blading. Materials which were satisfactory for the latter when low pressures and quite moderate superheats were the general practice, have proved quite inadequate to cope with modern conditions. Stainless irons and steels, however, have given very successful results under these conditions and, by now, the advantages following their use for blading have been generally recognised both by makers and users of turbines.

The selection of the most suitable type of stainless steel for some particular turbine or part of a turbine is a matter in which a number of factors are involved. Of particular importance are those relating to the various methods of fabrication employed by different turbine builders because these may modify radically the properties possessed by the steel as it leaves the steelmaker.

The properties desirable in a blade would appear to be, firstly, adequate strength (coupled with sufficient toughness and ductility) at the operating temperature to resist the forces set up during use ; secondly, the ability to retain its original shape and smooth surface, in other words, resistance to erosion and corrosion by steam. On these grounds, therefore, one would expect a fairly hard form of stainless steel to be a satisfactory choice. The matter, however, is much more complicated. Blading is always required to conform within narrow limits to some special section and the blades must be very firmly fixed in position in the turbine. The necessary section, within the prescribed limits, may be obtained by machining and when this is

combined with purely mechanical methods of fastening the blades, the problem presented to the steel manufacturer is in its simplest form. He can supply the steel he deems most suitable, for the particular set of conditions, in bar form heat treated so as to be in its best structural condition, with the comforting knowledge that the blading actually inserted in the turbine will possess this structural condition practically unchanged.

The machining of blading from bars is a costly and wasteful procedure ; as a result, cold rolling or drawing processes are being used to an increasing extent to obtain the necessary sections. Hence a further requisite of the steel to be used for blading so produced is that it shall be capable of being cold worked with reasonable ease to the sections required. And in order that the cold rolling or drawing may not be too long a process, it is desirable that the hot rolled bar supplied for these operations shall approximate in size and shape to the finished article.

As likely material for blading, the following groups of the stainless family may be suggested :—

(1) Stainless iron containing 12/14 per cent. chromium.

(2) Stainless steel of similar chromium but higher carbon content.

(3) Hardenable high chromium steel of the " Twoscore " type (16/20 per cent. chromium and about 2 per cent. nickel).

(4) Austenitic steels of the " V.2.A." family.

(5) Austenitic steels with a high nickel content, e.g., 20/40 per cent.

As regards ease of production in the form of hot rolled blading sections, stainless iron probably leads the way but all the first four groups are producible commercially in this form. Steels of class (5) offer more difficulty. Some steels of this class have been produced in hot rolled blading sections but of others the commercial production of hot rolled bars is limited to those of simple section, such as round, square or rectangular. The rather high initial cost of such material is therefore increased considerably in blade form owing to the necessity of using wasteful and expensive machining processes.

The relative ease of cold rolling or drawing the five groups of stainless steels depends on their initial hardness

and the rate at which they harden when cold worked. The first three groups are similar in the latter respect and hence in their case initial hardness is the determining factor ; the stainless irons are thus the easiest to handle and the others in order of their hardness. The austenitic steels of groups (4) and (5) are more difficult owing to their greater rate of work hardening ; this is perhaps the higher in those of group (4) but those of the other group have generally a greater initial hardness.

The methods of fastening blading in position next demand attention because those employed by turbine manufacturers frequently necessitate the blade being wholly or partly heated to high temperatures. For example, the vanes of fixed diaphragms are frequently held between a cast iron centre and rim, and the whole is assembled by casting the metal centre and rim round the vanes, which have previously been inserted in their proper positions in the moulds. During the casting operation, the vanes are heated to above the melting point of cast iron (approximately 1,150°/1,200° C.) and afterwards they cool down more or less rapidly, depending on the size of the diaphragm. In the case of turbines for marine work, the cast iron may be replaced by phosphor bronze ; the operation is similar except that the temperature is likely to be somewhat lower owing to the melting point of the bronze being about 1,075° C. If the blading material hardens to any great extent as a result of these " casting-in " processes, the vanes will be comparatively brittle.

The austenitic alloys do not harden at all when so treated and so would be quite satisfactory from this point of view, but unfortunately they suffer from certain defects which seem to render their use undesirable under such circumstances. In the first place, all these steels have normally a low yield point, and hence are liable to deform under relatively low stresses when in this condition ; hence the cold-rolling of blades of these materials is resorted to, not only as a convenient means of producing the required section but also to provide a stronger material. The idea is excellent providing it is remembered that the hardened blade thus produced must not be reheated to any temperature above about 450°/500° C., otherwise these enhanced mechanical properties are lost. This would obviously

occur in " cast in " blades. More important still, however, the " casting-in " process is likely to affect seriously the resistance of these steels to corrosion, owing to the precipitation of films of carbide round the austenite grains while the casting is cooling down. The rate of cooling of " cast-in " blades is not sufficiently rapid to avoid the formation of these carbide films, at least in the steels of group (4), and the requisite treatment to put the material in a proper condition (reheating to 1,000°/1,200° C. followed by rapid cooling) is obviously impossible as it would lead to the cast iron rim and centre being ruined.

Some of the austenitic steels with a high nickel content classified in group (5) are much less subject to intergranular weakness and these may be used successfully for " cast-in " blades, particularly those for marine work which are embedded in phosphor bronze.

In the case of stainless iron and the hardenable stainless steels, the requisite properties are obtained in a satisfactory manner by the use of such of these materials as contain not more than 0·15 per cent. carbon ; vanes with not more than this amount do not harden unduly when " cast-in." This may be illustrated by a series of tests designed to show the influence of carbon content on this requirement. Strips about 6 in. long, 1 in. wide and $\frac{1}{16}$ in. thick of steels containing respectively 0·10, 0·15, 0·18, 0·21 and 0·3 per cent. carbon were embedded in blocks of cast iron, about 12 × 3 × 4 in. The blocks were cast round the strips, the latter being placed in the moulds in such a position that a length of two inches of each was embedded in the cast iron in the manner indicated in Fig. 230. After casting, the blocks were allowed to cool down in the normal way for castings of such size. Prior to " casting-in," all the strips had been hardened and tempered in order to put them into a tough, ductile condition. After the castings had become quite cold, the projecting ends of the strips were bent through 90° at the points where they emerged from the block, as indicated by the left-hand strip in Fig. 230. All the strips of the steels containing 0·18 per cent. carbon or less stood this test successfully. Some of the strips containing 0·21 per cent. carbon also bent equally well, but others broke, and none of those of the 0·3 per cent. carbon steel could be bent in this manner without breaking. From these results,

a carbon content of not more 'than 0·18 per cent., or better 0·15 per cent., would appear to be desirable in the stainless material used for vanes treated in this manner. The lower limit is preferable as a measure of safety because the air-hardening capacity of these steels is affected by variations in their chromium and nickel contents.
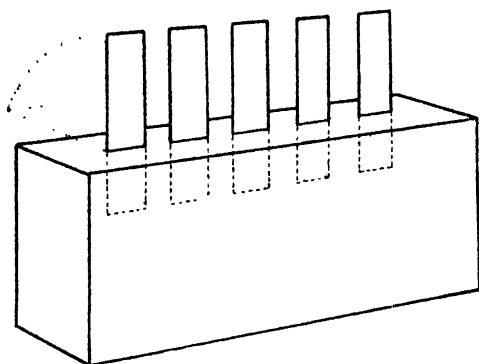
FIG. 230. Cast Iron Block and Stainless Steel Strips used for testing the effect of "Casting-in" on the hardness of the steel. See page 536.

A test of this nature, while giving the most certain information, has disadvantages as an inspection test for the supply of material. Experience over a number of years has shown that a satisfactory indication of the likely behaviour of different consignments of stainless iron and mild stainless steel may be obtained by an ordinary bend test carried out on strip which has been heated to 1,000° C., and then cooled freely in air. Strip 1 in. wide and ⅛ in. thick is convenient for testing and, after treating as suggested above, it should give a minimum bend of 60° over a radius of ¼ in. (i.e., 2T). The appropriateness of 1,000° C. as a testing temperature will be evident from curves " A " and " B " in Fig. 84, and " C " and " D " in Fig. 227, where the Brinell hardness numbers obtained from water-quenched samples of these materials are plotted against quenching temperature ; it will be observed that the hardness value reaches a maximum in the range 950°/1,000° C.

Considerations of air-hardening capacity should also be taken into account in selecting material which has to be brazed. Brazing may be used for actually fixing the

blade in position—in which case either part or the whole of the blade may be raised to the brazing heat—or for fastening the blades to shrouding rings or lacing wires, operations generally involving a local heating only. The temperature attained will depend on the particular brazing alloy used ; if this is the ordinary copper-zinc alloy, the temperature is likely to be about 950°/1,000° C. Special silver solders may be obtained, however, which melt at 700° C. or thereabouts, and with these a much lower temperature suffices.

From the point of view of absence of any induced hardness, austenitic alloys of group (4) would be admirable for brazing operations but, as in " casting-in," the effect on corrosion resistance may be serious ; hence the brazing of such steels is not generally advisable. Again it may be noted that some of the steels in group (5) are less subject to carbide precipitation and with these brazing is possible.

There is no difficulty in actually brazing stainless iron or the hardenable steels ; the point to be remembered is their relative air-hardening capacity. The higher carbon steels harden appreciably on cooling from temperatures of 800° C. and over, and hence in their case the use of the special silver solder is imperative and, in addition, the operation requires a considerable degree of skill in order to ensure that the steel is not heated above 800° C. In fact, it is very likely under ordinary workshop conditions, such as obtain in the brazing of lacing wires, that the thin edges of the blades would be heated above this temperature. Herein lies the value of the stainless iron, which may be heated considerably above 800° C. before it acquires any appreciable air-hardening capacity ; and even if it is heated to such an extent as to produce distinct hardening effects, it still retains sufficient ductility to bend satisfactorily, as was indicated in the paragraphs relating to " casting-in." It is possible to braze stainless iron with the ordinary copper-zinc mixture and obtain good results, but many engineers prefer to use the lower melting silver solder and thereby leave the material in the brazed portion of the blade in a tougher condition.

Summing up, it would appear that for blades to be brazed or " cast-in," the most suitable material to use is stainless iron. It is also the most easily fabricated by cold

working process and hence is particularly useful for the blading of reaction turbines. Such blading is generally thin, and, as there is often a great deal of it, it is generally cold rolled or drawn to shape. Many of the blades are long (hence the material should be tough) and as a result are brazed at several places to lacing wires. From all these points of view, stainless iron has satisfactory properties. On the other hand, when blading is machined to shape or is fixed in position by purely mechanical devices, such as occurs sometimes with the short sturdy blading of impulse turbines, a harder steel may be used (providing it is machinable), in order to obtain greater resistance to erosion, and there is no reason why it should not air-harden. In such cases a higher carbon steel, hardened and tempered to give a tensile strength 50/55 tons per square inch may be used to advantage.

Sometimes, instead of brazing the tips of the blades to a shrouding ring, they are passed through slots in the ring (which is often made of stainless steel strip) and then riveted over so as to form a tight fastening. This method is perfectly feasible with stainless iron and the austenitic steels and usually causes no difficulty with the hardenable stainless steels if the latter have a tensile strength not exceeding 50/55 tons per square inch.

It seems to be considered in some quarters, however, that in certain circumstances a more resistant material than the 12/14 per cent. chromium product is desirable. Under normal conditions, blading is subjected to the action of hot steam, wet or dry as the case may be, and, so far as may be judged from the results of several years' experience, stainless iron and steel with the above mentioned chromium content successfully meet these conditions. It is sometimes stated, however, that in marine turbines, for example, salt is liable to be carried over into the turbine, due presumably to the presence of some sea water in the boiler feed water. If this did occur, very severe corrosive conditions would result, particularly if the salt were deposited as minute crystals on the blades. During the periods when the turbine was shut down, these blades would be subjected to the action of moist salt crystals, a particularly virulent corrosive condition from which no form of stainless steel commercially available is entirely immune. Having regard to the measures which

may be taken te determine and control the alkalinity of feed water, it would hardly be expected that such conditions as are suggested above are likely to occur in a turbine under competent control but, regarding them as a possibility under less capable supervision, it should be pointed out that the 16/20 per cent. chromium steels of the " Twoscore " type are greatly superior to those of lower chromium content in their resistance to salt, and that the milder varieties of these steels (i.e., those with 0·1 per cent. carbon or so) behave in a similar manner, as regards air-hardening effects, to the stainless irons ; hence they may be substituted for the latter when their greater corrosion resistance is considered desirable.

The question as to what is the most suitable material for the blading of turbines using very highly superheated steam (e.g., 400° C. and over) is still a moot point. It has been stated that the 12/14 per cent. chromium steels are not sufficiently resistant under such conditions, though the author, in spite of many efforts, has not been able to discover the evidence on which such an opinion could be based. If it be assumed that the property which is alleged to be lacking is adequate strength at such temperatures—it is hardly likely to be resistance against corrosive attack by steam as the experiments detailed in an earlier chapter (page 331) indicate that the 12/14 per cent. chromium material has adequate resistance against such attack at 550° C.—then greater satisfaction is likely to be obtained from suitably chosen austenitic steels of groups (4) or (5), because these have a distinctly greater " creep strength " at such temperatures than the hardenable chromium steels. Whether this greater strength is really necessary or whether, in the case of some steels of group (5), it is obtainable at an economic cost, are questions to which satisfactory answers are not yet forthcoming.

In addition to the application of stainless steel in solving some of the problems met with in such distinct types of engineering work as steam and hydraulic service and turbine manufacture, there are many occasions arising in engineering or steel works where the use of stainless steel for some machine detail would result in a considerable saving, at least of trouble. For example, in the manufacture of railway tyres the steel for these is frequently cast in long ingots which are subsequently cut up, in powerful lathes, into blocks of the

necessary size. In two such lathes in use at the works the author is connected with, the tool holders are fitted with bolts, nuts and traversing pinions made of stainless steel ; by so doing, much trouble due to the rusting of similar parts made from ordinary steel, causing them to stick, has been avoided. In the same way, the main saddle taper wedges for the same lathes when made of ordinary steel were found to corrode at both ends, forming barrel-shaped wedges which caused the saddle to rock when the machine was at work. This has been avoided by making these parts of stainless steel.

Gauges may be made very effectively from a cutlery quality stainless steel ; although it may not be given so high a hardness value as carbon tool steel, it resists wear and abrasion exceedingly well and this, combined with its resistance to corrosion, makes it a very effective material for such tools. Parts of meters and other instruments, which are subject to corrosive effects during use, may be usefully made of one or other types of stainless steel ; very often the corrosion of some part of an instrument has a detrimental effect on the latter's accuracy and the elimination of this trouble is worth the extra cost of the steel.

Mining equipment is notoriously subject to corrosive attack. Damp atmospheres, sometimes containing deleterious gases, are often a feature of mining work and these have an extremely corrosive action on ordinary steels. Frequently mine waters contain acids and generally they contain much mineral matter in solution. Stainless steels, owing to their resistance against corrosive attack, offer great advantages under such conditions.

Stainless steels of various types have by now become standard materials for the construction of aircraft ; already a number of specifications, covering their supply, have been issued by the British Engineering Standards Association and the British Air Board. In most of these specifications, limits of analysis are prescribed and the material must also satisfy requirements as regards mechanical properties. For parts of machines subject to attack by sea water or spray, either the high chromium steels of the " Twoscore " type or the austenitic steels of the " V.2.A" class are selected on account of their greater resistance to corrosion. In other cases, the 12/14 per cent. chromium steels serve admirably.

Broadly speaking, the types of stainless steels used can be grouped in six classes.

(1) Material of a relatively low tensile strength required either in bar or sheet form for parts not subject to high stresses. Stainless iron is generally used in this case ; if greater resistance to corrosion is desirable, the fully softened austenitic steels may be employed.

(2) Medium tensile steel of the 12/14 per cent. chromium variety ; B.E.S.A. Specifications S.61 and S.62 cover the supply of such material, the carbon content of which is adjusted to suit the desired range of tensile strength (35/45 tons per square inch for S.61 and 46/52 for S.62). Material of this kind is used for a great variety of structural fittings which can be machined from bars, or forgings, which have been heat-treated to give the required mechanical properties.

(3) Steel supplied to B.E.S.A. Specification S.80, which calls for a hardenable steel having a chromium content of 16/20 per cent., combined with better mechanical properties than those mentioned above, namely a minimum tensile strength of 55 tons per square inch together with good ductility and toughness figures. This material is widely used for high stressed parts, subject to severe corrosive attack (e.g., in seaplanes and flying boats), which can be machined from heat-treated bars and forgings. Many aircraft firms use it as their standard material.

(4) Material in sheet or strip form supplied in the softened condition and required to give high values for proof stress after fabrication and heat-treatment.

Where corrosion conditions are severe, low carbon steel containing 16/20 per cent. chromium is used.* The sheet or strip is formed into various shapes (sometimes welded) and then heat-treated to give specified tests. Some typical values obtained from material of this kind are given in Table XXXII (page 152).

For parts where the corrosion resistance of the 12/14 per cent. chromium steels is adequate, material of this type containing about 0·15 per cent. carbon is used. Many of the spars of the ill-fated airship R.101 were made from

* British Air Board Specification D.T.D. 60 A.

steel of this composition ; the strip was formed by a patented process (with included heat-treatment) into light tubes of various sections which were used as spars. Some typical tests on strips of this type are given in Table CXXXIX.*

TABLE CXXXIX.

Mild Stainless Steel for Spars.

Tests on 20 *gauge strip, air hardened from* 1,000° C., *and then tempered as indicated.*

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Tempering Temperature.	Max. Stress. Tons per sq. inch.	0.1% Proof Stress. Tons per sq. inch.	Bend (180°) over
0.19	0.41	0.27	13.9	– –	450° C.	104.0	81.7	4.3t
					,,	109.7	80.4	4t
					500° C.	105.2	80.3	4t
					,,	104.2	78.4	3.8t
					525° C.	99.5	72.5	3.5t
					,,	99.7	69.4	3.5t
					550° C.	96.8	71.3	3.5t
					,,	95.5	70.8	2.9t
					575° C.	73.0	57.3	2.6t
					,,	73.8	62.0	2.6t
					600° C.	68.5	52.6	2.1t
					,,	67.1	55.0	2.1t
0.16	0.27	0.25	13.8	Trace	500° C.	109.2	85.0	3.5t
					,,	109.0	85.0	3.5t
					525° C.	105.0	81.5	8.5t
					,,	104.3	78.0	3.5t
					550° C.	99.8	73.8	3.25t
					,,	98.8	72.7	3.4t
					625° C.	76.7	63.2	2.2t
					,,	74.7	62.1	2.3t
0.20	0.80	0.24	13.6	Trace	500° C.	111.1	87.5	3.5t
					,,	110.4	86.3	3.5t
					525° C.	113.4	86.0	3.5t
					,,	111.1	85.0	3.5t
					550° C.	106.2	~77.7	3.5t
					,,	104.5	78.0	3.8t
					625° C.	77.7	62.8	2.0t
					,,	78.5	62.0	2.0t

(5) Cold rolled strip of austenitic chromium-nickel steel which can be formed into various parts without heating above 400° C., at the most. The strip is usually supplied to specifications calling for a minimum proof stress together with adequate ductility and is often used for the construction of spars and other parts which can be built up from strip. The fabrication of these must not involve heating over 400° C., otherwise the properties induced in the strip by cold rolling would be removed to a greater or less extent.

(6) Sheets for hulls of seaplanes and flying boats. Either the austenitic chromium nickel steels (fully softened) or low carbon steels of the " Twoscore " type may be employed. In either case the hulls are fabricated by riveting, the rivets being generally so small that they can be closed cold. Welding has not been used to any extent on account of the impossibility of heat-treating the whole structure after fabrication, but the advent of the new austenitic steels which are much less susceptible to intergranular attack (see page 288) may enable welded hulls to be constructed of such steels.

Corrosion is one of the most serious, and perhaps the most costly, problem confronting the chemical engineer, not only on account of the added cost of production due to replacement of equipment and stoppages for repairs, but also because of the possibility of contamination due to catalytic action or to the direct absorption of the products of corrosion of the equipment. It seems very probable that no single alloy will ever be produced which will offer a satisfactory degree of resistance to all chemicals. As will be gathered from the accounts given in Chapters V and VI, stainless steels are certainly not a panacea for all the corrosion ills and troubles which beset the chemical engineer, but their use is certain to afford him much help in dealing with many corrosive chemicals. Probably the outstanding example is in connection with the nitric acid industry ; many hundred tons of the steel have been used for the construction of plant for dealing with this acid. Similar help may be obtained by its use for other acid liquors such as those containing organic acids or the weaker mineral acids. For example, equipment for the dyeing of textiles offers wide scope for the

Plate LIII
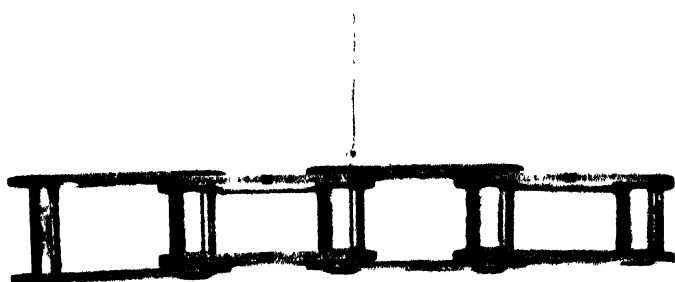
Fig. 231.   Part of stainless iron chain after running for the duration of a crushing season in a "Juice Strainer" see page 545
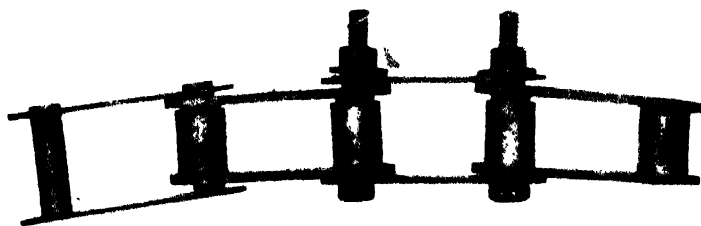
Fig. 232   Part of ordinary steel chain which ran alongside stainless iron chain shown in Fig. 231.

effective use of these steels.   Many dye liquors contain small amounts of sulphuric acid and a satisfactory degree of resistance to such liquor may often be obtained from the austenitic chromium-nickel steels.   Where the corrosive conditions are very severe, still better results are given from the more complex alloys, particularly those containing molybdenum.   The advantages of a metal vat, which is unattacked by the dye liquor, does not absorb the latter into its texture and hence may be readily washed free from one dye liquor before use with another, and withal has a smooth surface which will not injure a delicate fabric or yarn, should be apparent.

Equally great opportunities occur in the handling of salts and other more or less neutral bodies, either organic or inorganic, which constitute so large a part of the " heavy chemical " industry.   The longer life of plant, with its attendant savings due to decreased cost of upkeep and reduction of losses due to stoppages, together with the lessened risk of contamination of product, are advantages which make the employment of corrosion resisting steels profitable.   It is hardly necessary to give any detailed suggestions as to the possibilities in this direction ; they may be illustrated, however, by the result obtained by the use of a stainless iron chain in a " Juice Strainer " in the sugar industry.   Such chains are usually made of ordinary steel and they give considerable trouble owing to corrosion and rapid pitch extension.   Two such chains, which have the form shown in Fig. 231, were installed side by side and ran for the duration of a crushing season.   One chain was made of ordinary carbon steel, the studs, bushes and rollers being case-hardened ; the other was made entirely of stainless iron.   After the season's work, the stainless iron chain was found to have scarcely suffered ; the ordinary steel chain, on the other hand, was unfit for further use ; in fact, it had been necessary to insert bolts through the hollow studs to hold the side plates together in order that the chain might run to the end of the crushing season.   This is evident from the photographs Figs. 231 and 232, which show a short length of each chain at the end of the season's work.   Each piece is suspended by the middle joint and it will be seen that whereas the joints of the stainless iron chain are in good condition, those of the ordinary steel chain are very loose

and are only held together by the inserted bolts which are themselves appreciably corroded.

A word as to the selection of steels for chemical plant may not be out of place here. The vital factor is, of course, resistance to the particular chemical under consideration and this may limit the choice of suitable materials. Of almost equal importance, however, are the availability of the steels in the different commercial forms— e.g., castings, forgings, bars, plates, sheet, tubes, wire —in which steel is usually supplied and the ease with which they may be fabricated into various forms of plant.

Most chemical plant, constructed of ferrous materials, is fabricated by ordinary boilermaker's methods ; it is desirable therefore that materials used for the construction of such plant should have properties approximating as nearly as possible to those of mild steel, on which these processes have been developed. For this reason, chemical equipment is usually made from one or other of the following types of stainless material : --

(1) Stainless iron of either low or high chromium content.

(2) Austenitic chromium-nickel steels of the " V.2.A." type.

(3) Special austenitic steels, either of the " V.2.A." type modified by the addition of other metals (e.g., molybdenum, copper, tungsten, silicon) or else containing much more nickel than these.

Of these materials, types (1) and (2) are most generally used, those of type (3) being reserved, on account of their higher cost, for those particular cases where the simpler alloys do not possess adequate resistance.

It is not necessary to give here ·lists of chemicals for which these several classes of stainless steels may be used -- information in this respect has been given in earlier chapters— but it may be useful to deal briefly with their response to fabrication processes.

For purposes where a stainless iron (of appropriate chromium content) or an austenitic steel seem equally serviceable —and this occurs with the particular chemical, nitric acid, for which these steels have been most widely used—the choice between the two will be decided largely

by the method of fabrication to be adopted. If a riveted construction is desirable, the stainless irons have undoubted advantages ; they are more easily riveted and caulked than the austenitic steels. In the form of plates, they are also more easily bent, flanged or otherwise worked to shape. On the other hand, welded joints are much more satisfactory from a mechanical point of view in austenitic steels and when this method of construction is desired these steels are the better, provided always that either the welded vessel can be satisfactorily heat treated after the welding is completed or a suitable form of the steel can be obtained which has been proved by stringent laboratory tests (such as that suggested on page 287) to be free from intergranular weakness under the fabrication conditions to which it will be subjected. If either of these alternatives cannot be assured, it is better to abandon welding and use a riveted construction. In the case of a very large vessel, it may be possible to construct in sections, each of which may be heat treated after welding and then assemble these heat treated sections by riveting.

As a general rule, it is advisable to construct a vessel of one material only ; the risk of electrochemical action being set up if two different metals are in contact with each other is particularly great in chemical plant. Contact with non-ferrous metals should be especially eschewed ; for this reason, the use of brazed or soldered joints in the construction of stainless steel plant is generally undesirable. It may be noted, however, that no such ill effects appear to be produced by the contact of austenitic steels of the " V.2.A." family with stainless irons of similar chromium content if the two are exposed to nitric acid. Extended observations regarding this absence of effect have been made both in the laboratory and in actual plant experience and an explanation is probably to be found in the action of nitric acid in increasing passivity. Whether this be the cause or not, however, the absence of any deleterious electrochemical action under these conditions is exceedingly fortunate and valuable to the branch of the chemical industry concerned.

Local cold deformation should be avoided as far as possible in the construction of chemical plant, particularly that intended with very corrosive chemicals. Such cold worked areas are liable to be attacked not only on account of their lowered resistance, as indicated in Fig. 175 (page 292)

but also because they are apt to become electropositive to
the normal metal surrounding them, leading to selective
attack.   In the construction of tubular evaporators of the
austenitic steels, for example, the tubes should fit the holes
in the tube plates as closely as possible before expanding, in
order that the amount of deformation produced by the
latter operation may be as small as possible.   For the same
reason, the tubes themselves should be supplied in the fully
softened condition so that they may be expanded as easily
as possible and thus avoid the production of a highly distorted
skin on the inner surface of a hard tube in an endeavour to
produce a really tight joint.

The high coefficient of expansion of the austenitic steels
must be allowed for in plant constructed partly of these
materials and partly of mild steel.   A tubular evaporator,
for example, may be constructed of austenitic steel tubes
(and tube plates) fitted into a mild steel shell ; unless an
expansion joint is provided, considerable stresses will be set
up in the tubes and shell when the evaporator is heated.
For the same reason, austenitic steel tubes should be expanded
into tube plates of similar material ; if expanded into mild
steel, for example, it is unlikely that the joints would remain
tight after heating and cooling through any considerable
range of temperature.   Troubles of these sorts, however,
would not arise if stainless iron were employed as its co-
efficient of expansion is very similar to that of mild steel.

In all cases where parts of plant handling corrosive
liquors are subjected to alternating or repeated stresses, the
combined effects of corrosion and such stresses in lowering
the fatigue limits of steels (or other metals) must be very
carefully considered by designers.   Little data is yet avail-
able regarding the actual values of corrosion-fatigue limits
of metals in contact with specific chemicals but the data
given in Table CXVI show that, when immersed in sea
water, neither the austenitic steels of the " V.2.A." class nor
the stainless irons have fatigue limits greater than 10/12
tons per square inch.   It is probable that still more corrosive
fluids, for example those containing free acids, would reduce
the fatigue limits of these steels to still lower values.   At the
same time, the values given for stainless steels in Table
CXVI in regard to fresh water and sea water, though
apparently rather low, are still considerably higher than

Plate LIV .

Fig. 233. Towers of " Brearley K " stainless iron (16 18 per cent. chromium) erected on plant site Similar towers have also been erected in " 18 · 8 " chromium-nickel steel

Plate LI
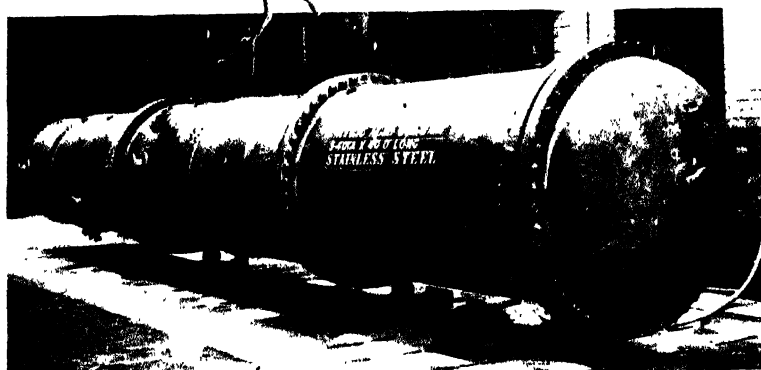
Fig. 234.—Stainless Iron column ("Brearley K") 16-18 per cent chromium under hydraulic test at 175 lbs. per sq. in.
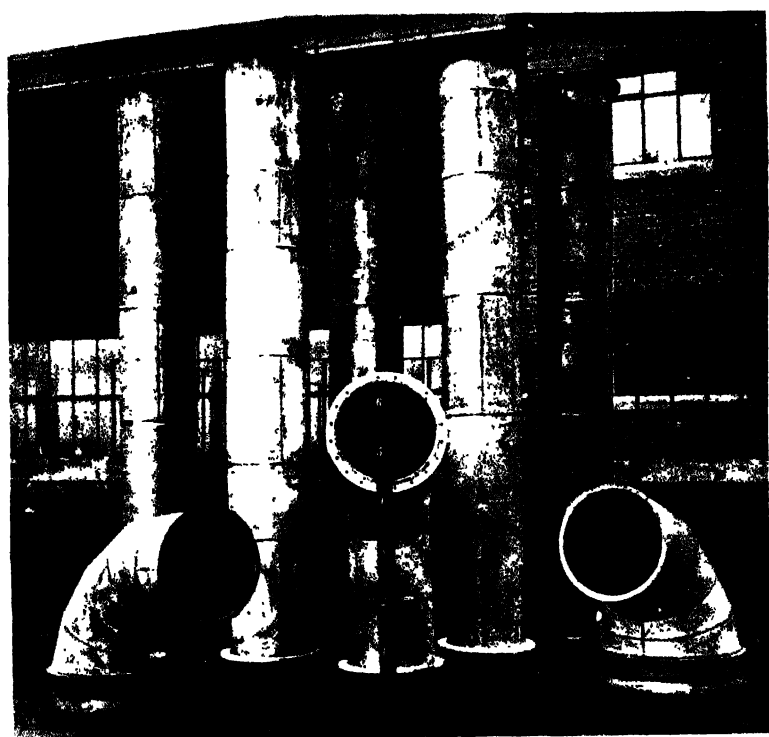
Fig. 235. Welded, heat treated and descaled tubes of chromium-nickel steel ("Anka").

those obtained from ordinary steels or the usual structural alloy steels ; on this account, the use of stainless steel for parts subjected simultaneously to fatigue and to corrosion by water, or other similarly corrosive fluids, will frequently lead to increased life.

The construction of large scale plant has progressed considerably during the last few years. The towers represented in Fig. 233 are typical of what can be done in regard to plant erected on the site. These two towers, of riveted construction, and erected at the Billingham works of Messrs. Imperial Chemical Industries Ltd., are noteworthy as they constitute, so far as the author's knowledge goes, the first large scale equipment of high (16/18 per cent.) chromium iron to be erected on the plant site. Previously the use of such high chromium irons had been confined to plant which could be fabricated in the boiler shop and then despatched complete to the plant site ; the fabrication of the two towers illustrated was rendered possible owing to the special properties of the " Brearley K " stainless iron to which reference was made on page 482. Towers of similar size and construction, but fabricated from austenitic steel of the " 18 : 8 " type, have also been erected at the same plant.

The tower illustrated in Fig. 235 (forty feet long and five feet four inches diameter), also constructed of " Brearley K " iron, was under test at a pressure of 175 lbs. per sq. inch at the time the photograph was taken. It is also of riveted construction, the plates being sixteen mm. thick, and is probably the first of its type to be made in Europe. The fact that it was fabricated without any trouble and with perfect success indicates the progress made in the construction of such plant.

The welded tubes shown in Fig. 236 were made of austenitic chromium-nickel steel (" Anka " brand) and were heat treated and pickled after welding. Their size may be gathered from the six foot rule placed in front of the centre tube.

These three examples are merely quoted to indicate that the fabrication of large scale plant has passed far beyond the experimental stage.

Questions have been raised at various times regarding the rather low values for thermal conductivity possessed by stainless steels—see Appendix, page 559,—and the possible

effect of this on the efficiency of heat exchangers and similar equipment constructed of these steels. Generally speaking, the effect is negligible, even when the steels are used in equipment previously constructed of copper. The reason is not far to seek. Heat exchangers are generally constructed of thin plates, sheets or tubes of metal and experiment shows that in transmitting heat through such thin metallic partitions from a liquid or gas in contact with one side to a second fluid in contact with the other side, at least 95 per cent. of the resistance to heat flow is due to films of liquid which cling to the metal surfaces. As a result, a plate of a metal with a relatively low conductivity, such as stainless steel, will in general conduct heat through its substance faster than the heat can be supplied to it by a liquid with which it is in contact. As some evidence of this, the following experiment may be quoted. A bar of copper 12 in. long and $1\frac{7}{8}$ in. diameter was drilled along its axis with a hole 5/16 in. dia. and 6 in. long. A thermocouple was inserted in this hole and metallic contact with the copper ensured by dipping the actual junction into a small amount of mercury previously placed at the bottom of the hole. The bar was then immersed in an ample supply of vigorously boiling water and the rate of heating of the thermocouple observed. The experiment was repeated with similarly prepared bars of mild steel, 12/14 per cent. chromium steel and an austenitic chromium-nickel steel with the results given in Fig. 237. In this experiment, the possible effects of differences in metallic conductivity were exaggerated, on the one hand by using bars of large diameter so as to give a long metallic path for the heat flow, and on the other hand by eliminating one liquid-metal inter-face and reducing the effectiveness of the other as much as possible by vigorous agitation of the water. In spite of this, the rate of heating of the thermocouple inside the austenitic steel bar was not much slower than that in the copper bar, as is evident from Fig. 237. When such precautions to ensure effective transfer of heat from liquid to metal were not taken, no difference in the behaviour of the steel and the copper could be detected. For example, when the copper and austenitic steel bars used for the last experiment were placed in a gas-fired furnace at 700° C., no difference in the rate of heating of thermocouples placed inside them could be detected. It is evident, therefore, that the

use of stainless steels in heat exchangers or similar equipment will not cause any loss of efficiency in the latter.*
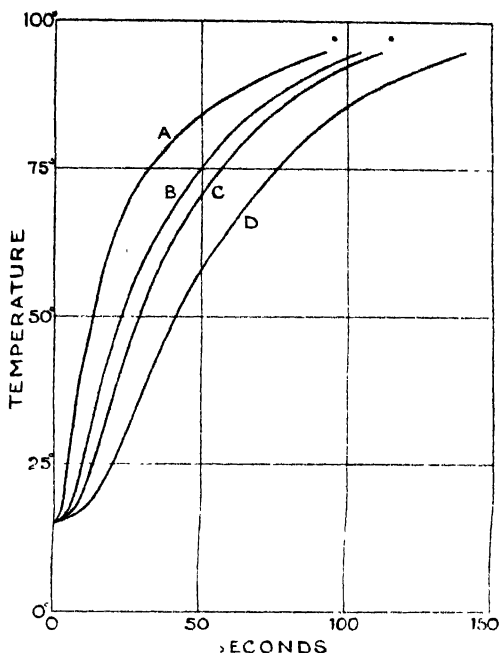
Fig. 236.   Rates of heating of bars (1⅜ in. diam.), immersed in boiling water; see page 550.

Curve A.   Copper.
  B.   Mild steel.
  C.   Stainless steel; 0·22 per cent. carbon ; 13·6 per cent. chror
  D.   Stainless steel; 0·16 per cent. carbon ; 16·1 per cent. chrom
    10·5 per cent. nickel.

Dairy equipment provides another very suitable outlet for the use of stainless steels.   From the point of view of resistance to the action of dairy products, stainless irons and the austenitic chromium-nickel steels are equally suitable ; they are completely unattacked by these products.   The austenitic .steels, however, are more resistant, to the acid cleansing fluids frequently employed in dairies and on this account have advantages.   A prime necessity in most dairy . equipment is the absence of nicks or holes in which the milk

* In connection with this, it may be noted that Worthington (*Chem. & Metal Eng.*, Aug. 1928, p. 481) reports that glass with a thermal conductivity one three-hundredth that of copper was found, in condenser experiments, to have one-third to one-half the heat transfer efficiency of copper.

or other product could lodge.* For this reason, particular attention must be given to producing perfectly smooth joints between sheets, etc., used in the construction of vessels. Generally this is attained by soldering; the solder must, of course, have a sufficiently high content of tin to be itself immune from attack.

In the oil industry, corrosion entails enormous expense; the crude oil contains sulphur compounds which cause rapid destruction of ordinary steels. The resistance of the high chromium and the chromium-nickel steels to attack under these conditions has already been profitably utilised to a considerable extent. Similarly, cracking equipment demands materials resistant to corrosive attack at high temperatures and also possessing considerable strength while heated. Again, one or other of the various types of corrosion-resisting steels have proved invaluable, the selection of the most suitable steels in specific cases depending on the conditions to be met, and these vary very considerably.

A similar multiplicity of operating conditions applies to the use of heat resisting steels generally. The requirements here are so varied that each problem must be examined on its own merits. Data regarding resistance to oxidation have been given in Chapter VII and where this property is the sole requirement, the problem is relatively easy. When it is complicated by the necessity for the selected material to have considerable strength at temperatures of about 800° C. and over and at the same time to be obtainable in seamless tube form, the metallurgical problem presented is one of very considerable difficulty.

For all these various purposes for which the use of stainless steel, in one form or another, is suggested, the relatively high cost of the material constitutes an obstacle which is becoming less serious as time goes on but is still of considerable proportions. The tendency to place an undue importance on the first cost of an article seems to be an instinctive trait of human nature; the author would suggest however, that cost in terms of service is a far better method of assessing values. If the rate of deterioration of stainless steel plant by corrosion, erosion or other form of attack, is so much slower than of similar parts made of ordinary steel (or other metals) that the increased life of the former more than compensates for its generally greater initial cost, its use will

obviously effect economies. ' In the case of the chains mentioned on page 545, against the greater initial cost of that made of stainless iron should be set the comparative freedom from the trouble and inconvenience (as well as actual loss) caused by the frequent renewal of corroded parts of machinery which is required to handle, in a limited time, large quantities of a natural product which must be dealt with as expeditiously as possible after it is ripe otherwise its value may depreciate considerably. The cost of the hydraulic valve described on page 532 was high but the economies due to elimination of stoppages alone exceeded this in less than a month. The more frequently the costs of corrosion problems are assessed in this manner, the greater will be the use of corrosion-resistant steels of one form or another. It is scarcely probable that the cost of even the cheapest of these steels will ever become as low as that of ordinary carbon steel or even approach this value. Their value, however, should be judged by the service they give and so long as their cost in terms of service is lower than that of ordinary steel, their use will prove advantageous to the engineer, chemical or otherwise, no matter what their initial cost may be.

APPENDIX

APPENDIX

SOME PHYSICAL PROPERTIES.

In compiling the following brief list of physical properties, results published by The Bureau of Standards, Dr. Hatfield, Dr. Mathews and others have been freely used. The admirable series of tables included in the Proceedings of the American Society of Testing Materials for 1930 and also the data published by several firms who manufacture stainless steels have also been drawn upon.

Density. Chromium lowers the density of steel to which it is added ; nickel raises it. Other metals which are occasionally present also act according to their respective densities ; thus copper, molybdenum and tungsten increase the density, whereas silicon and aluminium lower it. The

TABLE CXL.

Density of Stainless Steels.

Carbon %	Silicon %	Chromium	Nickel %	Tungsten %	Treatment.	Density.
0·35	0·23		—	—	O.H. 850°, T.650°C.	7·869
0·33	0·14	10·6	0·76	...	A.H.950°, T.700°C.	7·751
0·3	0·14	12·6	0·79	—	,,	7·738
,,	,,	,,	,,	—	A.H. 950°C. ...	7·731
0·08	0·25	12·3	0·26	...	A.H.950°, T.700°C.	7·779
0·08	0·24	15·4	0·30	—	,,	7·722
0·10	0·31	20·4	0·30	—	,,	7·683
0·25	—	27·5	—	—	A.C.700°C. ...	7·625
0·10	0·25	15·2	11·4	—	W.Q.1,000°C. ...	7·971
			,,	—	Cold worked to Brin. of 300/350	7·942
0·10	1·34	15·0	9·0	—	W.Q.1,000°C. ...	7·897
0·14	0·3	18·1	7·9	—	W.Q.1,100°C. ...	7·92
0·28	0·31	20·5	6·64	—	,,	7·870
0·24	0·26	20·2	8·4	—	,, ...	7·883
0·34	2·35	17·7	25·8	—	W.Q.1,000°C. ...	7·836
0·3	0·2	11·0	36·0	—	,,	8·05
0·47	·1·85	14·0	26·5	3·4	—	8·1
0·35	1·4	19·5	7·25	4·0	—	8·08

density of all steels is lowered slightly by cold work; that of hardenable steels is also affected by variations in carbon content or heat treatment, in a similar fashion to ordinary carbon steels.   Some typical values are given in Table CXL.

Co-efficient of Expansion.   The chromium steels expand at a rather slower rate than mild steel and distinctly more slowly than copper and the common copper alloys.   The austenitic steels, on the other hand, expand at about the same rate as copper.   Typical values for a number of materials are given in Table CXLI.

TABLE CXLI.

Co-efficients of Expansion.

Carbon %	Chromium %	Nickel %	Molybdenum %	Mean Co-efficient.				
				20°-100° C.	20°-200° C.	20°-400° C.	20°-600° C.	20°-1000° C.
* 0·3	13	—	—	(a)0·0000090	0·0000095	0·0000099	0·0000112	—
				(b)0·0000103	0·0000107	0·0000115	0·0000121	—
† 0·1	14	—	—	0·0000107	0·0000110	0·0000116	0·0000125	—
† 0·1	18	—	—	0·0000104	0·0000107	0·0000113	0·0000121	—
** 0·2	17·5	2·1	—	—	0·0000116	0·0000116	0·0000124	—
‡ 0·33	24·6	—	—	—	0·0000116	0·0000116	0·0000124	—
§ 0·2	28·0	—	—	0·0000102	—	—	—	0·0000134
** 0·1	15·4	11·2	—	—	0·0000180	0·0000184	0·0000186	—
† 0·1	18	8	—	0·000017	0·0000177	0·0000186	0·0000201	—
‡ 0·3	20·7	7·0	—	—	0·0000165	0·0000172	0·0000177	—
‡ 0·4	15·4	15·6	—	—	0·0000164	0·0000175	0·0000178	—
** 0·35	17·7	25·8	—	—	—	0·0000175	0·0000178	—
§ 0·2	25·0	17·5	—	0·0000162	—	—	—	0·0000202
‖ 0·3	11·0	26·5	—	0·0000167	—	—	—	—
‖ 0·3	11·0	36·0	—	0·0000136	—	—	—	—
¶ 0·2	19·0	10·0	3·25	0·000019	—	—	—	—
§§Pure Iron ...	....	...	...	—	0·0000126	0·0000138	0·0000147	—
*Mild Steel ...	...	...	...	0·0000111	0·0000116	0·0000133	0·0000143	—
*Monel Metal	...	...	...	0·0000143	0·0000147	0·0000159	0·0000162	—
§§Copper ...	...	...	..	—	0·0000167	0·0000179	0·0000187	—
§§Bronze ...	...	...	...	—	0·0000178	0·0000188	0·0000199	—
*Aluminium	...	...	...	0·0000237	0·0000248	0·0000268	0·0000293	—

(a) Hardened.
(b) Hardened and Tempered.
* Bureau of Standards.
† Dr. Hatfield.
‡ Dr. Mathews.

§ Allegheny Steel Co.
‖ Midvale Steel Co.
¶ Ludlam Steel Co.
** Author.
§§ Landolt Bornstein Tabellen.

Specific Heat.   Dr. Hatfield gives the following values :

Stainless steel	0·3% C. ; 12/14% Cr.	...	0·117
„ iron	0·1% C. ; 14% Cr.	...	0·115
„ „	0·1% C. ; 18% Cr.	...	0·115
Staybrite ...	18% Cr. ; 8% Ni.	...	0.117

APPENDIX.

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Similar values for the 18 : 8 composition are given by, for example, F. Krupp A.G. ; Republic Steel Corporation (U.S.A.) and Firth-Sterling Steel Co. (U.S.A.) but both the last two firms, and others in the States, give higher values for the chromium steels. The following values are taken from the A.S.T.M. tables referred to previously :—

Allegheny Steel Co. Stainless Iron, 14% Cr.   0.159
Austenitic Steel ; 0·2% C.
25% Cr. ; 17·5% Ni. ...   0.142
Carpenter Steel Co. Stainless Iron ; 13% Cr.   0.152
Republic Steel Corp.   Stainless Iron ;
13·5% Cr.   ...   ...   0·159
Firth-Sterling Steel Co. Stainless Iron ;
19% Cr.   ...   ...   0·151

Thermal Conductivity. There is some discrepancy between the data quoted by different firms ; as a whole, the results obtained in the States are higher than those given in this country or in Germany.   Some typical figures are given below :—

Type of Steel.	Source.	Thermal Cond.
0·3% C. ; 18% Cr.	Dr. Hatfield.	0·05
0·1% C. ; 12/14% Cr.... ...	,,	0·047
	Allegheny Steel Co.	0·096
	Republic Steel Corp.	0·097
	Firth-Stirling Steel Co.	0·096
0·1% C. ; 17/19% Cr.... ...	Dr. Hatfield.	0·082
	Republic Steel Corp.	0·052
	Firth-Sterling Steel Co.	0·072
0·1/0·2% C.; 18% Cr. ; 8% Ni.	Dr. Hatfield.	0·038
	F. Krupp, A.G.	0·04
	Allegheny Steel Co.	0·069
	Firth-Sterling Steel Co.	0·088
	Republic Steel Corp.	0·046
	Ludlum Steel Co.	0·052
0·2% C. ; 25·0% Cr. ; 17·5% Ni.	Allegheny Steel Co.	0·089
0·2% C. ; 19% Cr. ; 10% Ni. ; 3·25% Mo.	Ludlum Steel Co.	0·052
0·85% C. ; 11% Cr. ; 36% Ni.	Midvale Steel Co.	0·020
Silver	—	1·0
Copper	—	0·8/0·9
Pure Iron	—	0·14
Mild Steel	—	0·10/0·12

Electrical Resistance. Typical data are given in Table CXLII.

TABLE CXLII

	Carbon %	Silicon %	Man-ganese %	Chromium %	Nickel %	Treatment.	Resistance in Microhms per cm.³ at 15/20° C.	Temp-erature Co-efficient per ° C.
(a)	0·3	—	—	12/14	—	A.H.950°, T.700°C. A.H.950°/1,000°C.	50/55 65/70	— —
(a)	0·07	0·08	0·12	11·7	0·57	A.H.950°, T.700°C.	51	0·0016
(b)	0·08	0·5	0·5	13·5	—	—	59·8	—
(a)	0·08	0·33	0·15	20·7	0·27	T.700°C. ...	59·2	—
(c)	0·33	0·63	0·30	24·6	—	A.C.870°C. ...	68·5	—
(c)	0·30	0·67	0·56	29·8	—	„ ...	69·4	—
(a)	0·09	0·35	0·24	17·2	2·13	A.H.950°, T.650°C.	73·5	—
(a)	0·10	0·24	0·10	15·9	10·8	W.Q.1,000°C. ...	70·0	—
(d)	0·1	—	—	18	8	W.Q.1100°/1150°C.	69	0·00144
(a)	0·24	0·26	0·29	20·2	8·4	W.Q.1000°C. ...	71·2	—
(a)	0·16	0·23	0·80	11·7	23·9	„ ...	87·7	—
(c)	0·32	0·65	0·27	20·7	7·04	O.H.1200°C. ...	76·9	—
(c)	0·39	2·26	0·82	15·4	15·6	„ ...	93·0	—
(c)	0·41	1·84	0·80	7·3	22·6	„ ...	94·9	—
(c)	0·20	2·5	—	17·0	25·0	—	102·0	—
(e)	0·20	0·5	1·1	25·0	17·5	—	80·4	—
(f)	0·30	0·2	1·5	11·0	36·0	—	100·0	—

(a) Author.
(b) Republic Steel Corporation.
(c) Dr. Mathews.
(d) Dr. Hatfield.
(e) Allegheny Steel Co.
(f) Midvale Steel Co.

Magnetic Properties.

The following values are given by Dr. Hatfield and Dr. Mathews :—

Material.	B. max. H = 400.	B. rem.	Coercive Force.	Max. Perme-ability.
0·3% C. ; 13/14% Cr. (Hardened)	12,500	6,500	58	75
0·3% C. ; 13/14% Cr. (Soft)	17,150	12,800	13	650
0·1% C. ; 14% Cr. (Soft)...	17,170	6,100	7·5	500
" Staybrite "	—	—	—	1·01/1·03
	H = 150			
0·33% C. ; 24·6% Cr. OH. 1200°, T. 760° C. ...	12,450	5,720	11·4	312
0·30% C. ; 29·8% Cr. OH. 1200°, T. 760° C. ...	12,000	4,540	5·75	404

The 12/14 per cent. chromium steel makes a fairly good permanent magnet when hardened and may be used in this way when corrosion resistance is of importance. The austenitic steels are practically non-magnetic in the softened condition but bcoeme slightly magnetic when cold worked.

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